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# Evolution of hot fluids in the Chingshui geothermal field inferred from crystal morphology and geochemical data of veins

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## Abstract

The Chingshui geothermal field once hosted the first geothermal power plant in Taiwan between 1981 to 1993. After a long period of inactivity, this field is attracting renewed interest in order to meet the need for clean energy. A 213-meters length of cores (IC-21) with continuous recovery, the longest in the Chingshui geothermal field, were recovered from 600 m to 813 m below surface in 2010. Three types of calcite crystal morphologies have been identified in veins from the cores of well IC-21: bladed, rhombic and massive crystals. The bladed calcites are generated by degassing in boiling conditions with a precipitation temperature of  $\sim 165^{\circ}\text{C}$  and calculated  $\delta^{18}\text{O}$  value of  $-6.8\text{‰}$  to  $-10.2\text{‰}$  VSMOW for the thermal water. The rhombic calcites grew in low concentration  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  meteoric fluids and precipitated around  $\sim 180^{\circ}\text{C}$ . Finally, the massive calcites are characterized by co-precipitation with quartz in the mixing zone between meteoric water and magmatic or metamorphic fluids with

calculated  $\delta^{18}\text{O}$  value up to  $1.5\pm0.7$  ‰ VSMOW. Furthermore, the scales and hot fluids at a nearby pilot geothermal power plant confirm a meteoric origin. Based on these observations, we propose that the current orientations of the main conduits for geothermal fluids are oriented N10°E with a dip 70°E. This result provides the basic information needed for deploying production and injection wells in future developments of geothermal power plant in this region.

Keywords: Chingshui Geothermal field, clumped isotopes, fluid inclusions, calcite, formation scaling

## 1. Introduction

Minerals deposited in veins provide important records for studying the evolution of hot fluids in geothermal systems. Isotopic data from fractured-filling carbonate minerals have been found to be particularly useful to constrain the geochemical characteristics of fluid reservoirs and possible post-depositional and syntectonic fluid processes (Iwatsuki et al., 2002; Li et al., 2013; Luetkemeyer et al., 2016; Wallin and Peterman, 1999; Wang et al., 2010). Besides, the crystal morphology, which results from interaction of crystal surfaces and fluids during crystal growth, indicates not only their chemical composition but also the physical parameters relevant to crystallization including temperature, supersaturation, pressure, fluid dynamics and impurities in parent phases (Aquilano et al., 2016). Degassing during boiling is one of the most important factors controlling crystal morphologies in geothermal fields and ore deposits. Many studies have been published that discuss the relationships between

different kinds of crystal morphologies in non-boiling and boiling conditions (Bodnar et al., 1985; Canet et al., 2011; Griffiths et al., 2016; Harvey and Browne, 1992; Moncada et al., 2012; Pei et al., 2017; Simmons and Christenson, 1994; Tulloch, 1982).

The Chingshui geothermal field in northeastern Taiwan (Fig. 1) is an excellent case study for combining both crystal morphology and geochemical data to construct a hydrological model and to estimate fluid evolution in a geothermal system. There are many published geochemical and isotopic data from the hot fluids collected at the pilot geothermal production wells in the field (Chiang et al., 1984; Lin, 2000; Liu et al., 1990, 1982; Yui et al., 1993). The calculated  $\delta^{18}\text{O}$  values of hot fluids, based on calcite veins from outcrops and cores, were significantly different from that of discharged water from the wells suggesting different sources for the parent fluids of the calcite veins and current geothermal fluids (Lu et al., 2017). It is therefore important to assess conduit orientations and to construct a hydrological model for designing the production and injection wells in the future development of geothermal power plants in the Chingshui geothermal field.

There are 213 meters (depth 600-813m) of continuous core recovered from borehole IC-21, which is the longest core in the Chingshui geothermal field. Abundant calcite veins with different orientations and crystal morphologies were identified and collected for geochemical analyses. In this paper, we use crystal morphologies, isotopic compositions ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values), and temperatures from fluid inclusions and clumped isotopes of calcites to understand the calcite precipitation conditions in the wells and outcrops, and then to evaluate the parent sources and orientations of fluid conduits in the Chingshui geothermal field. The aim

of this study is to construct a hydrological model for designing the production and injection wells in the future development of geothermal power plants.

## 2. Background

### 2.1 Geological setting

The Chingshui geothermal field is located in the Valley of Chingshui River, approximately 13 kilometers southwest of the Ilan Plain, northeast Taiwan (Fig.1). The geothermal field is hosted in argillite/slate of the >3,000 meters-thick Miocene Lushan Formation (Hsiao and Chiang, 1979; Liu et al., 1986; Tseng, 1978). The Lushan Formation has been regarded as a fracture-controlled geothermal reservoir. The meteoric water seeps down through fractures to depth, then is heated to over 200 °C, and finally flows back to the surface through the fault-controlled conduits (Chen, 1982; Liu et al., 1990, 1982; Yui et al., 1993). Although some researchers have advocated this model (Ho et al., 2014; Hsiao and Chiang, 1979; Lin and Lin, 1995; Lu et al., 2016; Tseng, 1978; Wu and Chiang, 1976), the regional geological structures were mainly inferred from geophysical data due to poor outcrops and are still unclear and controversial (Chang et al., 2014; Hsiao and Chiang, 1979; Su, 1978; Tong et al., 2008).

Two major regional faults named the Xiaonanao fault and Chingshuishi fault, and a few small unnamed ones, cut through rock bodies in this area. The Xiaonanao fault has wide fractured zones and is rich in quartz veins with euhedral crystals along the Chilukeng River, while the Chingshuishi fault was only deduced from geophysical data. Several researchers correlated the fractured zones in the Chilukeng River with

the gouges at the Hanshi River and viewed the Xiaonanao fault as a south-dipping thrust associated with Plio-Pleistocene Orogeny (Hsiao and Chiang, 1979; Tseng, 1978). Meanwhile, other researchers suggested that there was a third fault cutting through the Chingshui geothermal field, named 'G fault,' based on fracture distributions from drilling and geophysical data (Huang and Chuang, 1986) (Fig.1). Lu et al. (2017) reported a series of north-dipping small normal faults with strike-slip parallel to the Xiaonanao fault, which are associated with abundant calcite veins (square in Fig.1). These observations imply that the normal faults might be associated with the latest phase of the Okinawa Trough opening (Kimura, 1985).

Thermal structure and hydrological circulation of the Chingshui field are still controversial. Lee et al. (2012) proposed cold water recharge from higher altitude anticline fractures to the south, and heated by high geothermal gradient, finally upwelling along the Chingshuishi and G faults. However, Chang et al. (2014) reported that the Chingshuishi Fault and the smaller faults with south dipping parallel to the Xiaonanao fault that are hypothesized to act as water infiltrating fractures are in fact an upwelling permeable zone as demonstrated by magnetotelluric Surveys (MT).

## 2.2 Hydrological background

In the Chingshui geothermal field, the hot water is characterized by a high concentration of  $\text{HCO}_3^-$  (up to 2,768 ppm) and low  $\text{Cl}^-$  (lower than 40 ppm) with pH values between 8.5 and 9.0, and the non-condensable gasses being predominantly composed of  $\text{CO}_2$  (up to 98%) (Lin, 2000) (Table 1). Under these conditions, carbonates would have been precipitated easily when the geothermal reservoir was opened by tectonic activity or drilling for geothermal exploitation. The  $\text{CO}_2$  is oversaturated and released quickly by depressurization causing rapid bicarbonate oversaturation with pH increase leading to rapid precipitation of carbonate minerals.

There is abundant scaling inside the wells and pipelines which precipitated during power production in this area, and was also interpreted by simulation using the TOUGH2 code (Zhang et al., 2015).

### 2.3 Overview of the pilot Chingshui geothermal power plant

A reconnaissance survey of this geothermal field was performed by the Industrial Technology Research Institute (ITRI) from 1973 to 1975 (Lee, 1994). Further exploration was subsequently conducted by the Taiwan Chinese Petroleum Corporation (CPC), and then a 3 MW pilot geothermal power plant was constructed in the field by the National Science Council (NSC) in 1981. It had been operated for 12.5 years and then was shut down due to a rapid decline in power production, which was caused by widespread scaling in production pipes (Lin, 2000; Lu et al., 2011).

In 2005, the Bureau of Energy of Taiwan restarted geothermal exploration in Taiwan and proposed a plan to develop geothermal energy for future power generation in the Chingshui geothermal field. The Ministry of Science and Technology (MOST) (formerly the National Science Council, NSC) of Taiwan has initiated and promoted geothermal exploration and development as Major National Energy Projects (NEP I & II) since 2008. The works include more precise geological, geochemical and geophysical surveys with drilling (Song, 2012). A 1,158-meter deep production well, named IC-21, was drilled into the reservoir of argillite/slate host rocks. Continuous core 213 m long, between 600 m to 813 m depth, was retrieved in 2010.

A brand new power plant is to be constructed in the geothermal field. The Ilan County Government initiated a ROT (Rent-Operate-Transfer) project for the Chingshui geothermal power plant in 2016 due to Taiwan's growing needs for clean

and renewable energy. According to the contract, this plant should have at least 1MW power generation in 2020 and over 3MW in 2022. A hydrological model, thus, is an important and emergent task for deploying the production and injection wells in this region.

### **3. Samplings and Analytical Methods**

#### **3.1 Core descriptions and sample information**

A total of 87 carbonate veins in cores from 600-813 meters depth in the IC-21 well were sampled for analysis. The vein information including depths, minerals, and relative orientations were obtained (APPENDIX A. SUPPLEMENTARY DATA 1). The relative orientations of veins were recorded respectively to the dip direction of slaty cleavage in the core. Assuming that the orientations of slaty cleavages at depth are the same to that of the surface, we can re-orient the veins to a true geographic orientation. Two sets of slaty cleavages were observed at the surface nearby the IC-21 drilling site (APPENDIX A. SUPPLEMENTARY DATA 2). The averages of two measurements in cleavages orientations of slates are N70°W with dip 69°S and N70°W with dip 70°S, respectively. Therefore, we assumed the strikes of cleavages in this area is to be N70°W, and recalculate the vein orientations in the cores.

Crystal morphologies of calcite were observed under a transmitted light optical microscope (OM) and a Scanning Electron Microscope (SEM). Element compositions of calcite were confirmed by Energy-dispersive spectroscopy (EDS) in the Department of Geosciences National Taiwan University. The mineral phases of veins were determined by X-ray diffraction analysis (XRD) at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan.



## 3.2 Carbon and oxygen isotopic analyses

A subset of 81 samples was selected for carbon and oxygen isotopic analysis. These were conducted using a Thermo Scientific MAT 253 Isotope Ratio Mass Spectrometer (IRMS) at the Institute of Oceanography, National Taiwan University. The isotopic compositions were normalized to the Vienna Pee Dee Belemnite (V-PDB) for  $\delta^{13}\text{C}$  and the Vienna Standard Mean Ocean Water (V-SMOW) for  $\delta^{18}\text{O}$ . The  $\delta$  notation is defined as:

$$\delta (\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$$

R is the ratio of either  $^{13}\text{C}/^{12}\text{C}$  or  $^{18}\text{O}/^{16}\text{O}$ . The analytical precision ( $1\sigma$ ), based on replicate analyses of the carbonate standards, were 0.03 ‰ and 0.06 ‰ for carbon and oxygen isotopes, respectively.

## 3.3 Clumped isotope analysis

Clumped isotope analysis was conducted at the Qatar Stable Isotope Laboratory at Imperial College London. The details of the sample preparations and analytical procedure have been published in [Lu et al., \(2017\)](#) and [Kluge et al., \(2015\)](#). All of the data processing was performed using “Easotope,” a software program designed for complex isotope analysis ([John and Bowen, 2016](#)). The parameters used for processing the data were followed procedures highlighted in [Schauer et al. \(2016\)](#) and in [Daëron et al. \(2016\)](#) to avoid problems with  $^{17}\text{O}$  correction. The calcite precipitation temperature calculated from corrected  $\Delta_{47}$  values were based on experimental calibrations by [Kluge et al. \(2015\)](#) adapted for the new  $^{17}\text{O}$  correction. The  $\delta^{18}\text{O}$  values of fluids were estimated using the equation by [Friedman and O’Neil \(1977\)](#).

The clumped-isotope  $\Delta_{47}$ -temperature relationship has initially mainly been applied to paleoclimate research (e.g. Daëron et al., 2011; Eiler, 2011; Ghosh et al., 2006; Tripathi et al., 2010; Zaarur et al., 2011). However, more and more researchers shift their attention to high-temperature applications (e.g. Bergman et al., 2013; Cruset et al., 2016; Dale et al., 2014; Kele et al., 2015; Luetkemeyer et al., 2016; MacDonald et al., 2016; Shenton et al., 2015; Sumner et al., 2015). Kluge et al. (2015) established a calibration curve between 25°C and 250°C using precipitation experiments mixing  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  in a pressurized reaction vessel at pressures of up to 80 bars. Lu et al., (2017) calculated a clumped-isotope temperature of  $214 \pm 16^\circ\text{C}$  from the IC-13 scales of Chingshui geothermal field using the equations of Kluge et al. (2015), which is within error but slightly higher than the well logging temperature ranging from 187°C to 210°C. Accordingly, the  $\Delta_{47}$ -T equation calibrated by Kluge et al. (2015) is validating the use of this calibration for the well conditions.

The massive calcites are opaque at  $100\ \mu\text{m}$  thick under microscopy and it is difficult to determine the formation temperature using fluid inclusions. The clumped isotope temperatures provide useful information for those carbonates which we could not estimate previously using fluid inclusions.

### 3.4 Fluid inclusion thermometry

Homogenization temperatures were measured on fluid inclusions in highly transparent calcite and quartz crystals from the veins of the cores at the Fukuoka University of Japan. Doubly polished wafers  $100\ \mu\text{m}$  thick were measured on a USGS heating and freezing stage, and the accuracy is within 1 % relative error of the measured temperature based on calibration using the SYN FLINC synthetic fluid

inclusion. The heating rate is about 3°C/min, and slower when it is approaching homogenization temperature.

## 4. Results

### 4.1 Orientation, mineral assemblages and crystal morphology of veins

The dominant orientations of IC-21 veins are around N10°E to N20°E with a steep dip towards the east. Some veins are oriented S70°E and S30°W and dipping to the south and west, respectively. It is difficult to determine the orientations of a small number (9/81) of veins from the IC-21 well due to irregular geometry. More than half of IC-21 veins (56/81) are predominantly composed of pure calcite, while the others (25/81) consist of mixtures of calcite and quartz (APPENDIX A. SUPPLEMENTARY DATA 1).

Three kinds of crystal morphologies of calcites in IC-21 veins have been recognized with naked-eye and microscopic observations: massive, rhombic and bladed (Fig.2). The most common one is massive calcite, which was often co-precipitated with quartz. Mosaic contacts observed under the back-scattered detector SEM images (Fig.3a), which show that the calcite and quartz were precipitated at the same time. Moreover, bent- and thick-twins are often found in massive calcites (Fig.4a). Occurrences of those massive calcites with quartz are found as kink structures and veins. Their orientations vary from N10° to 20°E dominantly (Fig.5a). There are also some massive calcites without co-precipitated quartz, which show opaque appearances and well-developed twin structures with dominated orientations of N10-20°E in the veins (Fig.5d).

Many macroscopically rhombic calcites infilling vugs (Fig.2b) were identified in the cores. They often occur as crystal clusters without twin structures on the surface of twinned massive calcites (Fig.3b). The main orientations of rhombic calcite crystals are also N10 to 20°E (Fig.5b).

The macroscopically bladed calcites mainly occur in near-vertical fractures (Fig.2c), and fillings of hydraulic-breccias (Fig.2d) at depth intervals of 627-633 m, 680-681m, 690-692m, 713-714m, and 743-745m, and 760-762m (Fig.6c). Those depths corresponded to depths with lower values on sonic (DT) and resistivity (Res) logs (Fig. 6a) (Liu et al., 2013). The size of these crystals reaches to 8 mm. The microscopically bladed calcites can also be found on the top of veins under SEM (Fig. 3c). It should be noted that the sample R92-3 (the number 92 is the drilling run and the number 3 the section of core) is different to other samples with lattice structures. It is characterized by aggregates of numerous parallel platy crystals (Fig.2e). Detailed descriptions of samples are shown in APPENDIX A. SUPPLEMENTARY DATA 1.

#### 4.2 Carbon and oxygen isotopic analyses

Carbon and oxygen isotopic analyses indicate that calcite veins from the Chingshui outcrops and scaling in geothermal wells IC13 and IC19 have the highest and lowest values recorded from the Chingshui geothermal field.  $\delta^{13}\text{C}$  values from the Chingshui outcrops range from -1.9 ‰ to -0.3 ‰ while  $\delta^{18}\text{O}$  values range from 8.3 ‰ to 17.8 ‰ (Fig.7) (Lu et al., 2017).  $\delta^{13}\text{C}$  values from scaling in wells IC13 and IC19 range from -7.9 ‰ to -7.0 ‰ while  $\delta^{18}\text{O}$  values range from 2.8 ‰ to 4.86 ‰ (Fig.7) (Lu et al., 2017). Isotopic compositions of calcite veins from the drilled cores of well IC-21 plot between those of Chingshui outcrops and scaling from wells IC13 and IC19, measured by Lu et al., (2017). They range from -6.8 ‰ to -1.5 ‰ and 0.8 ‰ to

14.4 ‰ for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively (APPENDIX A. SUPPLEMENTARY DATA 1, Fig. 7). In detail, most of the rhombic and bladed calcites have more depleted carbon and oxygen isotopic values than those of massive calcite (Fig. 7), ranging from -6.5 ‰ to -3.4 ‰ and 1.8 ‰ to 8.1 ‰ for  $\delta^{13}\text{C}$  VPDB and  $\delta^{18}\text{O}$  VSMOW, respectively.

#### 4.3 Clumped isotope analysis

The  $\Delta_{47}$  values of massive and rhombic calcites collected from IC-21 cores are  $0.415 \pm 0.001$  ‰ and  $0.422 \pm 0.005$  ‰ ( $\pm 1\text{SE}$ ), which translates to clumped isotope temperatures of  $208 \pm 14^\circ\text{C}$  and  $173 \pm 16^\circ\text{C}$ , respectively, using the temperature calibration of Kluge et al. (2015). Accordingly, the calculated  $\delta^{18}\text{O}$  values of the original thermal water are  $+1.5 \pm 0.7$  ‰ and  $-4.0 \pm 1.0$  ‰, respectively when using the equation of Friedman and O'Neil (1997) (Table 2).

#### 4.4 Fluid inclusion thermometry

All observed fluid inclusions in calcites and quartz are predominantly composed of two-phase liquid and vapor at room temperature without any daughter minerals (Fig. 8). The homogenization temperatures of rhombic calcites are distributed widely, ranging from  $166^\circ\text{C}$  to  $235^\circ\text{C}$ , which is higher than that of bladed calcite with temperatures between  $152^\circ\text{C}$  and  $180^\circ\text{C}$  (Fig. 6e, Table 3). The homogenization temperature of massive calcites is not easy to measure because of their opacity in host crystals, so the co-precipitated quartz sample (R100-1) was measured instead. The quartz recorded homogenization temperatures ranging from  $179^\circ\text{C}$  to  $254^\circ\text{C}$  (Fig. 4, Table 3).

### 5. Discussion

## 5.1 Formation of crystal morphology

### 5.1.1. Bladed calcite

Bladed calcites with skeletal structures have often been reported in epithermal and geothermal systems (André-Mayer et al. 2002; Canet et al., 2011; Harvey and Browne, 1992; Moncada et al., 2012; Pei et al., 2017; Simmons and Christenson, 1994; Tulloch, 1982). Simmons and Christenson (1994) first reported evidence of boiling of fluid inclusions by coeval vapor-rich ones and Th-Tm plotted figures. The rapid CO<sub>2</sub> loss caused by boiling triggers a quick crystallization of calcite, favoring the formation of the tabular habit, referred to here as bladed calcite.

Macroscopic bladed calcites occur only at a depth shallower than 762 meters of IC-21. These observations suggest that carbon dioxide began to degas from the system at depths shallower than 762m below the surface in the Chingshui geothermal field. The vugs and fractures filled by bladed calcites are almost near-vertical orientations (Fig. 2c). It can be interpreted that the steeply dipping conduits have the highest possibility to connect to the surface, thus promoting rapid boiling. Some bladed calcites have also been found in the matrices of hydraulic breccia (Fig. 2d). This evidence indicates that if the fractures opened suddenly, the pressure drop and degassing occurred quickly to ‘explode’ the host rock and precipitate the bladed calcites immediately.

Bladed calcite has also been documented in the Broadlands-Ohaaki geothermal field of the Taupo volcanic zone in New Zealand (Simmons and Christenson, 1994; Tulloch, 1982). The bladed calcite in Broadlands-Ohaaki shows clear series-parallel flake crystals, with cross-sectional zones in each bladed calcite crystal showing alternating layers of fluid inclusion-rich and overgrowth inclusion-free zones. In

comparison, in the IC-21 cores from the Chingshui geothermal field, some of the bladed calcites show parallel flake structures (Fig. 3d1), but most of the bladed calcites are elongate plate shapes (Fig. 3d2). All of the fluid inclusions are scattered inside the bladed calcite without connecting to the crystal surface (Fig. 8a). We, thus, identified that all of the fluid inclusions are primary inclusions.

In the Chingshui geothermal field, most of the fluid inclusions in the bladed calcites are liquid rich inclusions (Fig. 8a) but show wide range variations of homogenization temperatures. A few vapor-rich inclusions have also been observed (Fig. 8a), which suggest that boiling occurred and resulted in bladed calcite formation.

#### 5.1.2. Rhombic calcite

The macroscopically rhombic calcite in the IC-21 core is characterized by diamond shaped crystal structure. It grows on the top of massive calcites and fills up in natural vugs in the IC-21 core. No twin structures have been observed in massive calcites to suggest that those crystals were not subjected to any stress effects.

Generally, the rhombic calcites preferentially form at lower concentrations of  $\text{CO}_3^{2-}$  and  $\text{Ca}^{2+}$  ions as they have the minimal difference in surface potential between crystal faces, resulting in the rhombic morphology (Domingo et al., 2006; Lahann, 1978; Moore and Wade, 2013). However, higher concentrations of  $\text{CO}_3^{2-}$  and  $\text{Ca}^{2+}$  ions with over-saturation has been detected in the well fluids and the Chingshui river water (Table.1). We, thus, speculate that the meteoric water was heated and mixed by steam derived from deeper hot fluids to precipitate rhombic calcites in the cracks.

#### 5.1.3. Massive calcite

Massive calcites are the most abundant calcite morphology and are found in kink structures and veins with various orientations in core IC-21. Their occurrences are similar to the calcite veins of outcrops near the Xiaonanao fault (Lu et al. 2017). They appear as milky opaque crystals under optical microscopy with twin structures (Fig3a). Many thick twins ( $>1\mu\text{m}$ ) with bent twins and twinned twins have been found in massive calcite veins. These are thought to form at temperatures of  $150^{\circ}\text{C}$  to  $300^{\circ}\text{C}$  with significant deformation in syn-tectonic events, as proposed by Burkhard (1993) and Ferrill et al. (2004).

Meanwhile, some of the massive calcites occurred together with euhedral quartz crystals in the IC-21 veins indicate that a drop in temperature might also have played as important a role as degassing when the hot fluids rose up to shallower depths. We, therefore, propose that the veins consisting of massive calcites with quartz were formed during tectonic activity associated with stress changes. When the hot fluids were injected into the shallower fractures, boiling would occur in the fractures and the calcite and quartz could precipitate simultaneously (Fig.3a).

There are also some massive calcites not co-precipitated with quartz but are characterized by well-developed twin structures, which indicate they are formed by rapid degassing related to tectonic activity. Meanwhile, the carbon and oxygen isotopic compositions of those samples are scattered in between two end members of outcrops and scaling (Fig. 7). This evidence suggests that the origin of massive calcites might have multiple processes. The massive calcite without quartz occurs in steeply-dipping fractures, which suggest they are conduits which connect to the surface and therefore induce pressure decrease rather than temperature decrease. Accordingly, the isotopically enriched fluids were injected upwards from depth to



rapidly precipitate calcite without quartz. However, those massive calcites with isotopically lighter values and twin structures could be generated from heated meteoric fluids, and subjected to later tectonic activity to form the twin structures.

## 5.2 Crystal forming temperature

The IC-21 drilling project suffered from serious well collapse events and left drilling rods inside forever. Therefore, the well temperatures shown in Fig.6b and Fig.6d were measured inside rods (Lee et al., 2016), which can be view as final temperature but without detailed depth temperature correction. Accordingly, the borehole temperatures of IC-04 are used for supplement and comparison (Fig. 6b and 6d). Well IC-04 is located less than 20 m from well IC-21, which was the highest production well (~114.3 ton/hour) for the pilot geothermal power plant during 1976 to 1993.

The homogenization temperatures ( $T_h$ ) of fluid inclusions and well-logging temperature are shown in Fig.6e. The lowest  $T_h$  of bladed calcites, around 165 °C, is similar to the measured temperature in well IC-21. However, most of the lowest  $T_h$  of rhombic calcites are higher than the present measured temperatures by about 10-20 °C (Fig.6d, Table 3).

Both the fluid inclusion and clumped-isotope temperatures have been done in the same sample, R76-2. The results show that the lowest  $T_h$  and the calculated clumped isotope temperature are 186 °C and  $173\pm16^\circ\text{C}$ , respectively, which both are higher than the measured temperature, 160 °C . The massive calcites recorded higher temperatures than the well temperature, the  $T_h$  of quartz co-precipitated with massive calcite being 179-254°C . Meanwhile, the corresponding clumped isotope temperature of massive calcite is  $208\pm14$  °C based on the equation of Kluge et al. (2015). Those

data suggest that the bladed calcite has crystallized recently at current geothermal conditions, while the rhombic and massive ones may have precipitated from hotter fluids previously present in the Chingshui geothermal field.

[Passey and Henkes \(2012\)](#) reported that calcite is precipitated from fluids with different susceptibilities of C–O bond reordering which record their crystallization history. The more rapid the cooling rate, the shorter the precipitation time, which is from  $10^{-6}$  to  $10^{-2}$  degrees per annum. This may explain why the lowest  $T_h$  is higher than the clumped isotope temperature in sample R76-2. The  $T_h$  recorded the temperature of calcite precipitation, while the clumped isotope temperature recorded the cooling process, both of which are higher than presently measured temperature. Those evidence may suggest that the Chingshui geothermal field is on a waning stage of the system.

Conversely, we observe that the parallel platy calcite in sample R92-3 has a much lower  $T_h$  than measured present-day well temperature, which is the opposite of our measurements on massive calcites. The lowest  $T_h$  and measured temperatures are  $152^{\circ}\text{C}$  and  $162^{\circ}\text{C}$ , respectively. This reverse temperature relationship suggests that the parallel platy calcite may be precipitated from hot fluids from depth mixed with cold water from nearby shallower fractures. Although we did not have a detailed temperature profile along the depth in IC-21 due to drilling rods broken inside the hole, it can be supported from the temperature logging from IC-4 ([Fig. 6b](#) and [6d](#)), which shows a temperature drop of about  $5\text{--}10^{\circ}\text{C}$  in several depth intervals.

### 5.3 Isotopic data and fluid sources

Two end members of carbonates have been recognized by isotopic data in the Chingshui geothermal field. One is the calcite veins near the series of north-dipping

small normal faults which have enriched  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values ranging from -1.9 ‰ to -0.3 ‰ and 8.3 ‰ to 17.8 ‰, respectively. The other is the scaling in geothermal wells having  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  from -7.9 ‰ to -7.0 ‰ VPDB and 2.8 ‰ to 4.86 ‰ VSMOW (Fig.6), respectively. The calculated  $\delta^{18}\text{O}$  values of fluid are  $-1.0\pm1.6$  ‰ to  $10.0\pm1.3$  ‰ VSMOW from outcropping calcite veins and  $-5.8\pm0.8$  ‰ VSMOW from scaling in the well (Lu et al., 2017).

According to Lu et al. (2017), those calcite veins with heavy carbonate isotopic values were precipitated from fluid dominant in magmatic or metamorphic origins, which show  $\delta^{18}\text{O}$  values ranging from +5.5 ‰ to +10.0 ‰ and +5 to +25 ‰, respectively (Taylor, 1974). Moreover, The rock formation underneath the Lushan Formation is a pre-Tertiary basement that is predominantly composed of marble (Ernst, 1983). The  $\delta^{13}\text{C}$  values of this marble range from 0 ‰ to +4.0 ‰ (Chu and Shieh, 1981; Yui and Lan, 1991), which is higher than the local meta-sandstone in the Lushan Formation, which ranges from -3.2 ‰ to -2.5 ‰ (Lu et al., 2017). The decarbonization of marble could result in heavy carbon isotopic values in the magmatic or metamorphic thermal fluids.

The calcite scaling with more depleted carbonate isotope values are formed under meteoric water dominant conditions. The  $\delta^{18}\text{O}$  value of thermal water and steam from geothermal plant range from -4 ‰ to -6.7 ‰ and -11.6‰ to -8.0‰ VSMOW, respectively (Liu et al., 1990). Those of dissolved inorganic carbon (DIC) in geothermal water range from -8.5 ‰ to -7.5 ‰ (Liu et al., 1982).

Most of the rhombic and bladed calcites have lower carbon and oxygen isotopic values and are closer to the end member of scaling from the pilot geothermal production pipes (Fig. 7). If we calculate the  $\delta^{18}\text{O}$  value of fluid by  $\delta^{18}\text{O}$  value of calcite and lowest  $T_h$ , the  $\delta^{18}\text{O}$  value of fluids range from -10.2 to -3.8 ‰ VSMOW

(Table 3). Those values almost overlap in the thermal water and steam of geothermal plant (Liu et al., 1990). Those light  $\delta^{18}\text{O}$  values indicate that the fluids which precipitated bladed calcite and rhombic calcite may have a meteoric origin with differing amounts of mixing with steam condensed water (Fig. 9).

On the contrary, the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of massive calcites are scattered and closer to the end member of veins around the faults in the Chingshui geothermal field. These suggest that the hot water responsible for massive calcite formation comes directly from magmatic or metamorphic fluids or mixing of such fluids with meteoric water in different proportions during polyphase tectonic events.

There are a few datapoints of crystal morphologies and carbonate isotopic values that do not follow the general trends as the aforementioned observations. Sample R53-3 is composed of massive calcite and euhedral quartz with extremely light  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values being -6.8 ‰ VPDB and 0.8 ‰ VSMOW, respectively (Fig.7). Those morphologies with “feathery structures” or “flamboyant structures” on quartz crystal (Fig. 4b) indicate that they are formed during boiling condition of the fluids (Dong and Zhou, 1996; Moncada et al., 2012). The irregular shapes of veins in the sample of R53-3 also suggest that they might be formed at extreme situations with strong degassing and temperature drop due to tectonic activity.

On the contrary, sample R30-1 consists of rhombic calcite with heavy carbon and oxygen isotopic values (Fig.7). Vein orientation of this sample is N70°W with 82°S dip, which is different from the main fluid conduits of N10-20°E. It suggests that a tectonic event with a different stress field orientation may have occurred before the present stress field in the Chingshui area. This event produced the fractures

connecting to the deep reservoir, in which the fluid is characterized by heavy oxygen isotope values (Lu et al., 2017).

#### 5.4 Conduit orientations for thermal fluids

Current thermal fluids for the pilot power plant in the Chingshui geothermal field come from heated meteoric water, which has the most negative  $\delta^{18}\text{O}$  values of those measured/calculated from Chingshui (Liu et al., 1990, 1982; Lu et al., 2017). They are easily distinguished from hot fluids at depth, which are characterized by heavier oxygen isotope values. Our results indicate that the calcite veins with extremely light  $\delta^{18}\text{O}$  values were precipitated from the heated meteoric water.

Almost all of the veins with bladed and rhombic calcites have relatively light  $\delta^{18}\text{O}$  values (Fig.7), confirming precipitation from shallow, heated meteoric water. The opened fractures with orientations of N10-20°E, now filled by calcites with lighter  $\delta^{18}\text{O}$  values, are the conduits for fluid flowing currently (Fig.10). Moreover, bladed calcites and rhombic calcites occurred at depths with lower sonic (DT) and resistivity (Res) log responses, corresponding with the current fracture system (Fig. 6a).

On the contrary, the veins predominantly composed of massive calcites sometimes associated with quartz may be derived from the fluids of the deep reservoir, which is characterized by the heavier  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values, mixing with shallow meteoric water in different proportions. Those massive calcites may also be precipitated in deeper fractures, and then uplifted to shallow depths. The uplift rate of Chingshui area is around 2-4 mm/yr (Kang et al., 2015). Accordingly, the calcite veins with different crystal morphologies and isotopic ratios from the IC-21 cores may allow us to understand the current conduits of ascending thermal water in the Chingshui geothermal field.

Two sets of conjugate joints have been measured in the field. One is N25-40°W with dipping 75-90°E, and N25-30°E with dipping 75-80°W, while the other is NE-N10°E dipping 80-90°E and N60-70°W dipping 65-80°W (Tseng, 1978). The latter is consistent with our measurements from the IC-21 well. Meanwhile, an Anelastic Strain Recovery (ASR) method for in-situ stress measurements on the cores of IC-21 has been done immediately following core recovery. The results show that the current stress state is NE-compression and NW-extension of strike-slip faulting in the Chingshui area (Yeh, et al., 2013). It implies that the cracks with NW orientation must be closed ones, while NE-trending cracks could act as conduits for current fluid flow (Sun and Yeh, 2013; Yeh et al., 2013).

Three possibilities for fault orientations related to the N10-20°E conduits have been proposed (Fig.11). They are N10-20°W, N40-50°E, and co-existing N10-20°W and N40-50°E. The orientation of N10-20°W is consistent with the Chingshuishi fault, while the N40-50°E coincides with a series of normal faults observed by Lu et al. (2017) (Fig.1). However, there is no strong and decisive evidence to support which fault plays the dominant role at current conduits.

Geochemical tracer tests using tritium were done by the Industrial Technology Research Institute (ITRI) of Taiwan during 2010 to 2011. Tritium tracer was injected into a well located at the most northward site (hole IC-9). Almost no tritium concentrations higher than background were detected (ITRI, 2011). However, sodium benzoate injected at IC-21 could be detected at IC-19, which is located to the north of IC21 (ITRI, 2012). Furthermore, the  $\delta D$  and  $\delta^{18}O$  values of geothermal water range from -58 ‰ to -47 ‰ and from -7.4 ‰ to -5.7 ‰, respectively, which are considerably lower, by 20 ‰ in  $\delta D$ , than those of the local river and creek waters. Such results suggest that the recharge area for the thermal water may be located at

higher altitude, southeast of the study area (Liu et al., 1990, 1982). We, therefore, suggest that the meteoric water recharging the deep reservoir may come from the SE, an area with higher altitude than the Chingshui geothermal field (Fig.11). On this basis, we recommend that the injection wells should be deployed and drilled in the southeast of this area.

## 5.5 Formation of scaling

A 3 MW pilot geothermal power plant was constructed in the Chingshui geothermal field in 1981. After operating for 12.5 years it was shut down due to a major decline in hot fluid production and was considered not economically viable in 1993. Much calcite scaling was found inside the pipes, which was likely an important reason for the declining discharge of thermal water. Acidic solutions, therefore, were used to remove the scaling every two years (Lin, 2000). This treatment was useful to increase production, but soon after the re-start of the production, discharging rate decreased over the course of several runs. This result may imply that the scaling formed not only in the pipes but also in the fractures of the reservoir due to the degassing by discharging hot fluids. This could rapidly precipitate bladed calcite and therefore explain why we found many different grain sizes of bladed calcites on the surface of veins under SEM and naked-eye inspection of core IC-21. However, very few calcite veins were found in well IC-04, the first production well in this geothermal field (Huang and Peng, 1976). Additionally, no bladed calcites have been reported at outcrops near IC-04. This suggests that the calcite veins observed in the Chingshui drilled cores may have been precipitated after discharging large amounts of thermal water for power generation.

## 6. Conclusion

Three kinds of crystal morphologies of calcite have been recognized in the IC-21 veins: massive, rhombic and bladed calcites. The massive calcite with/without quartz is characterized by opaque milky color and thick twin structures with relatively heavy carbon and oxygen isotopic values and precipitation temperatures higher than 200 °C. It tends to form at greater depths via ascending fluids during tectonic activity, generated from the mixing of magmatic or metamorphic fluids and meteoric water in different proportions. The rhombic calcites are transparent and have lighter carbon and oxygen isotopic values, and are interpreted to have precipitated from a fluid dominantly composed of meteoric water with relatively low  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  concentrations during aseismic periods. The bladed calcite with lattice structures indicates that rapid degassing occurred in open cracks connecting to the surface during seismic faulting or the rapid discharging of hot water for the pilot geothermal power plant. The veins in open cracks of N10-20°E with dip 70°E may be of heated meteoric water origin as indicated by oxygen isotopic data, which are the same as scaling precipitated by hot fluids in the geothermal power plant. We, therefore, propose that the main orientation of the flow channel is N10-20°E from south to north. This result provides the basic information to design the production and injection well deploying in near future developments of geothermal power in the Chingshui geothermal field.

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**Fig. 1.** (a) The Chingshui geothermal field (red star) is located in the southwest of Ilan Plain, an area formed during back arc extension of the Okinawa Trough. (b) The red dashed box is the main hot water upwelling zone in the Chingshui area. Three major faults, the Xiaonanao, the Chingshuishi, and the G faults, and several subsidiary normal faults with strike-slip components (black box) have been found in this area. The drilled wells, such as IC-04, -09, -13, -16, -19, and -21 are predominantly distributed in a 1.3 km<sup>2</sup> by the Chingshui River.

**Fig. 2.** Photographs of the calcite morphologies observed in the veins of IC-21 cores: (a) massive, (b) rhombic, (c) bladed calcites in fractures, (d) bladed calcites in breccias, and (e) parallel platy calcite. The diameters of one and ten dollar coins are 2 and 2.6 centimeters for scales.

**Fig. 3.** Scanning electron microscopy (SEM) images of calcite morphologies observed in the veins of IC-21 cores: (a) massive, (b) rhombic, (c) bladed calcites on the surface of rhombic calcite, and (d) cross-section view of bladed calcite. (d1) bladed calcites with series-parallel flake crystals, and (d2) bladed calcites are one-layer platy shapes.

**Fig. 4.** (a) Photomicrograph of massive twinned calcites intergrown with quartz. Yellow arrows denote bent twins. Blue arrows indicate thick twins with twinned twins. (b) Photomicrograph showing feathery structures in sample R53-3, denoted by the yellow arrows.

**Fig. 5.** Vein orientations in lower hemisphere projections show that veins of N10–20°E with steep inclinations are widely distributed in all crystal morphologies. Orientations of massive calcites with quartz (a) and without quartz (d) have wider variations than that of rhombic calcite crystals (b) and bladed calcites (c).

**Fig. 6.** (a) The sonic logging (DT) and resistivity (Res) in IC-21 (Liu et al., 2013). (b) The geothermal gradient of IC-04 borehole temperature (light blue to dark blue are 8 hours, 24 and 48 hours after drilling) and the temperature inside the drilling pipe of IC-21(Gray), respectively. (c) The bladed calcites appeared shallower than 762 m in depth of the IC-21. (d) The plot of oxygen isotopes vs. depth shows that there are no relationships between the oxygen isotopes with

depth. (e) The temperature profile from depth of 600-820 meters, showing measurements of homogenization fluid-inclusion temperatures for bladed calcites (blue), rhombic calcite crystal (orange) and quartz crystal of massive sample (purple).

**Fig. 7.** Plots of carbon and oxygen isotope values of calcite veins and scaling from outcrops and wells in the Chingshui geothermal field, showing data from this study and from [Lu et al., \(2017\)](#). Results show that calcites from outcrops and scales from wells IC-13 and IC-19 are end members in the system. Vein calcites from well IC-21 are widely distributed in between these end members. The bladed calcites and most of the rhombic calcite crystals have lighter  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values than those of massive calcites with/without quartz.

**Fig. 8.** Optical microscope images of fluid inclusions in the bladed calcite of R57-2(a) and rhombic calcite crystals of R127-3(b). The bladed calcite microscope image shows considerable variation of gas/liquid ratios in inclusions. Red arrow denotes a gas-rich inclusion while the blue arrow highlights a fluid-rich inclusion, which suggests that a relatively slight boiling occurred.

**Fig. 9.** The calculated  $\delta^{18}\text{O}$  values of hot fluids associated with rhombic and bladed calcites are close to meteoric water mixing with steam condensed liquid, while the  $\delta^{18}\text{O}$  values of fluids derived from massive calcite are much heavier than that of the local meteoric fluids. The latter may be mis temperatures of fluid inclusions in bladed and rhombic calcite, and clumped isotopic temperature for massive calcite.

us temperatures of fluid inclusions in bladed and rhombic calcite, and clumped isotopic temperature for massive calcite.

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**Fig.10.** Relationships between  $\delta^{18}\text{O}$  values of calcites and vein orientations. The lighter  $\delta^{18}\text{O}$  values are predominantly distributed in the fracture orientation of N10-20°E.

**Fig.11.** Three scenarios showing the fractures related to the framework of strike-slip faults assuming that N10~20°E is the main orientation of geothermal conduits. They are (a) ~N10-20°W, (b) ~N40-50°E, and (c) co-existence of N10-20°W and N40-50°E.

**Fig.12.** Conceptual model of geothermal conduits in the Chingshui geothermal field. Two fault systems with orientations of N10-20°W and N40-50°E developed the main conduit with an orientation of N10-20°E.

**Table 1.** Geochemical data of the composition of fluids sampled from wells

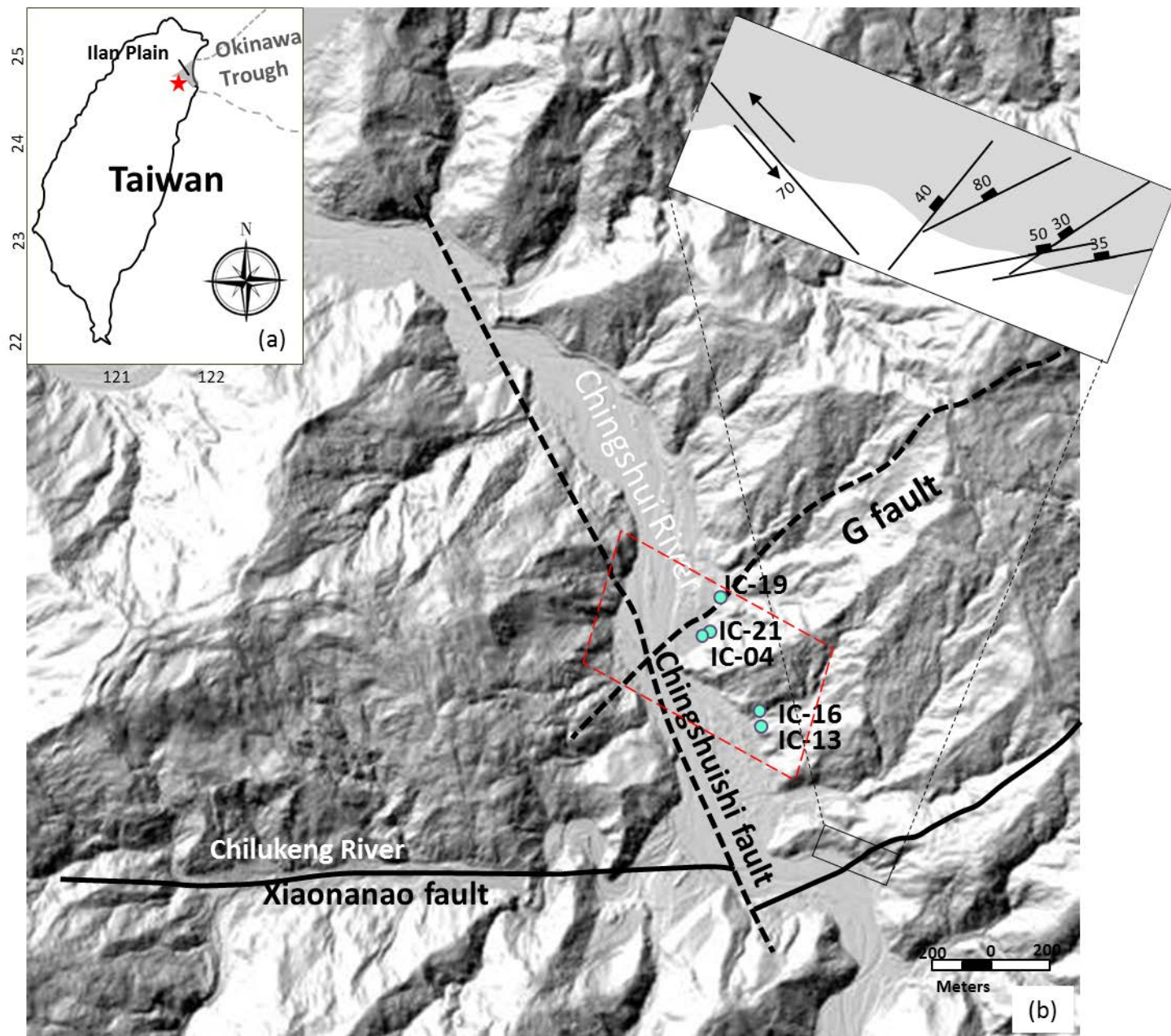
**Table 2.** Clumped isotope data and the calculated  $\delta^{18}\text{O}$  VSMOW of parent fluids.

**Table 3.** Homogenization temperatures of fluid inclusions and the carbonate isotope values.

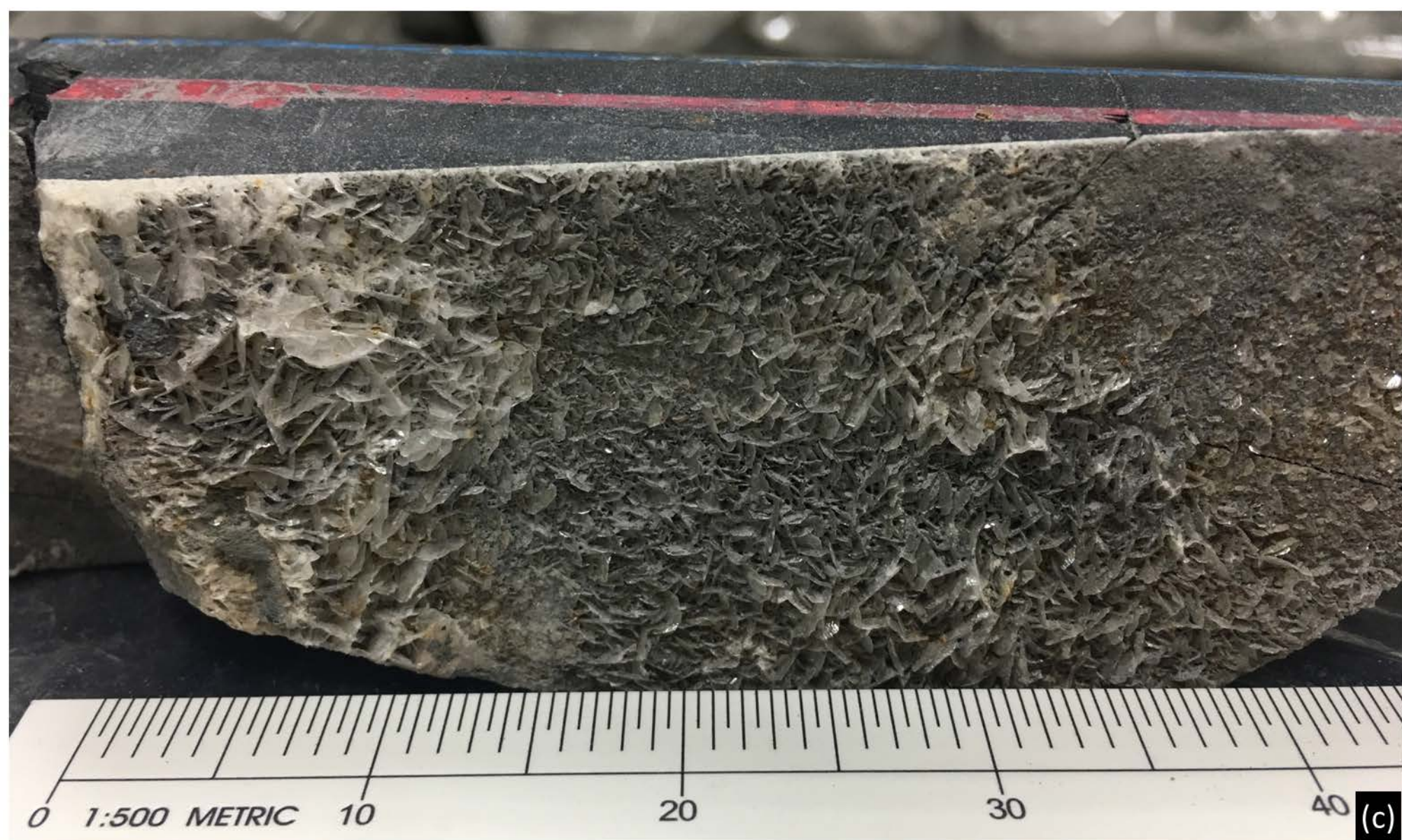
**APPENDIX A. SUPPLEMENTARY DATA 1. Carbon and oxygen isotopic data**

**APPENDIX A. SUPPLEMENTARY DATA 2. Slaty cleavages measured at surface outcrop nearby the IC-21 drilling site in Chingshui geothermal area**

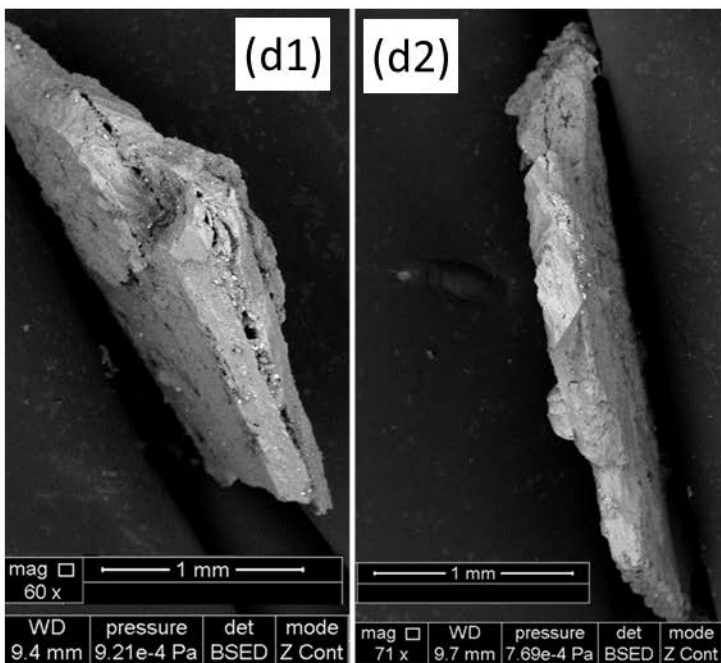
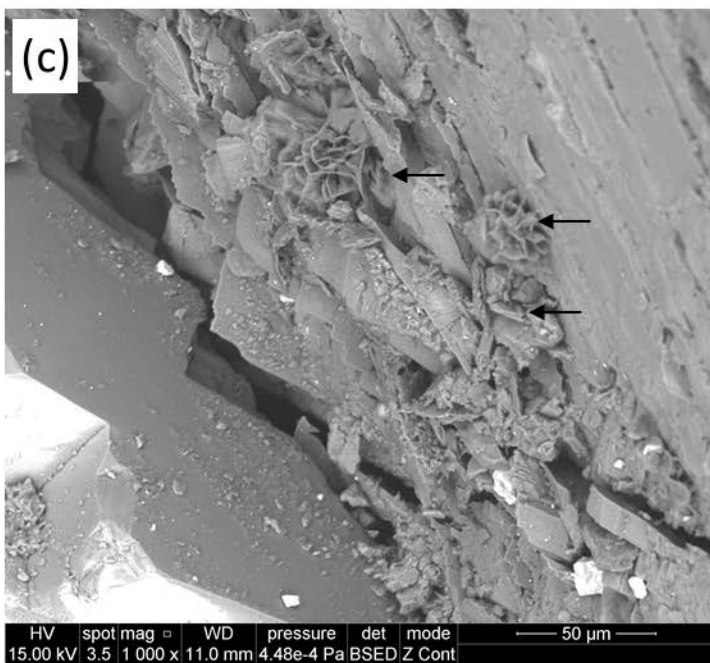
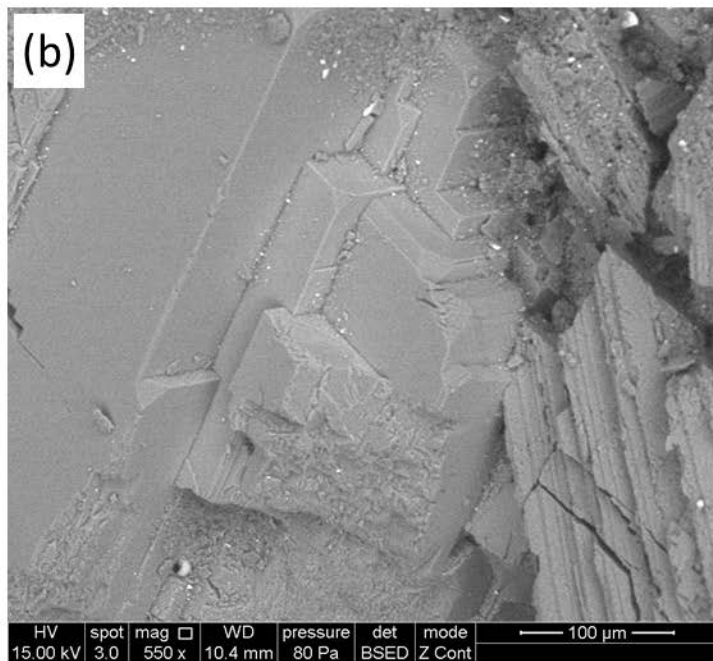
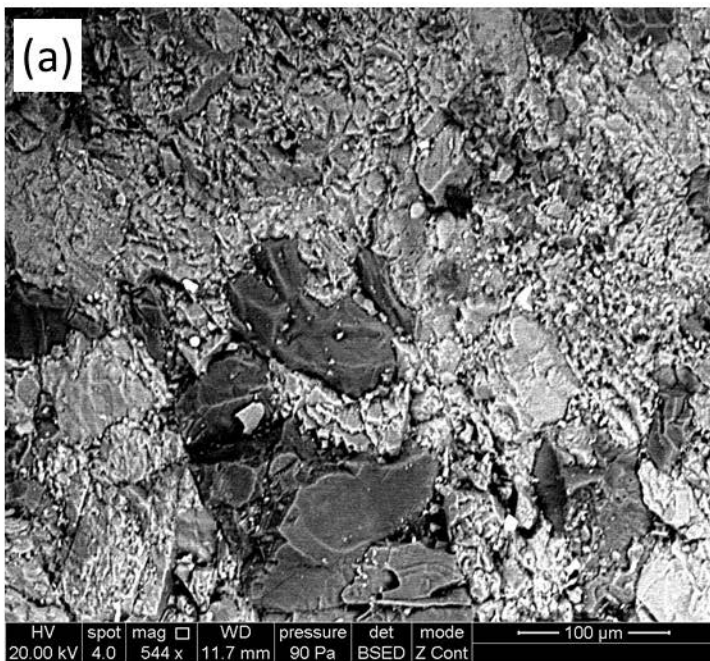
**APPENDIX A. SUPPLEMENTARY DATA 3. Fluid inclusion data**

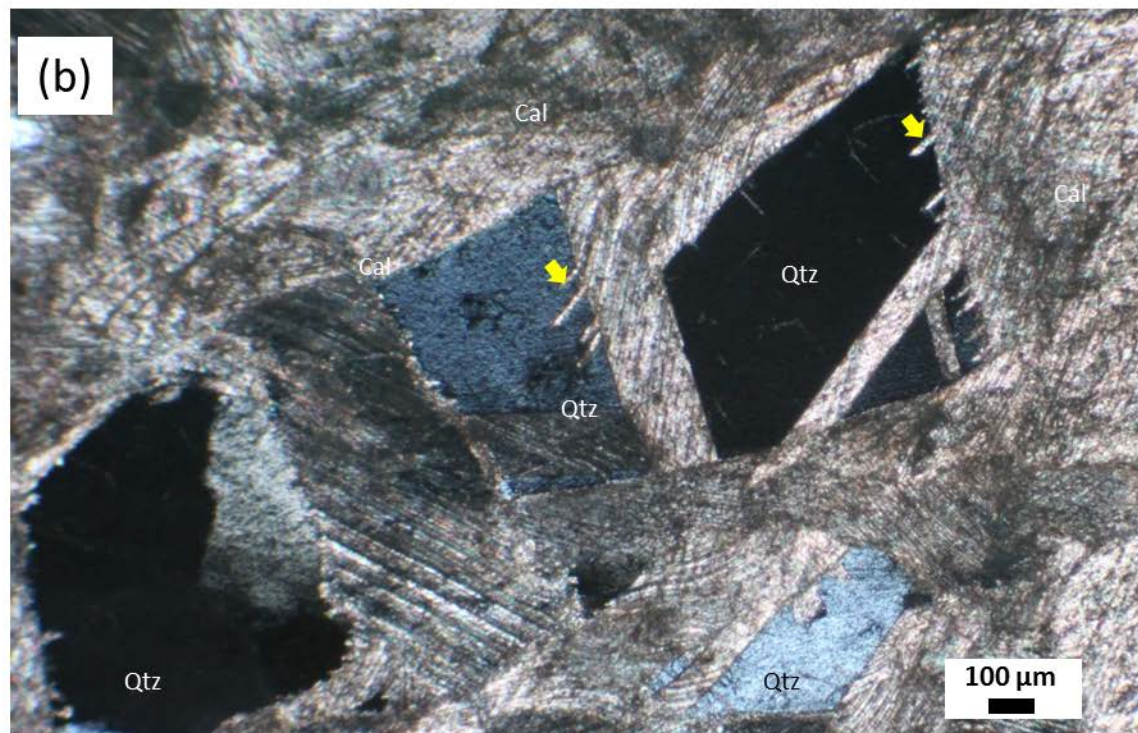
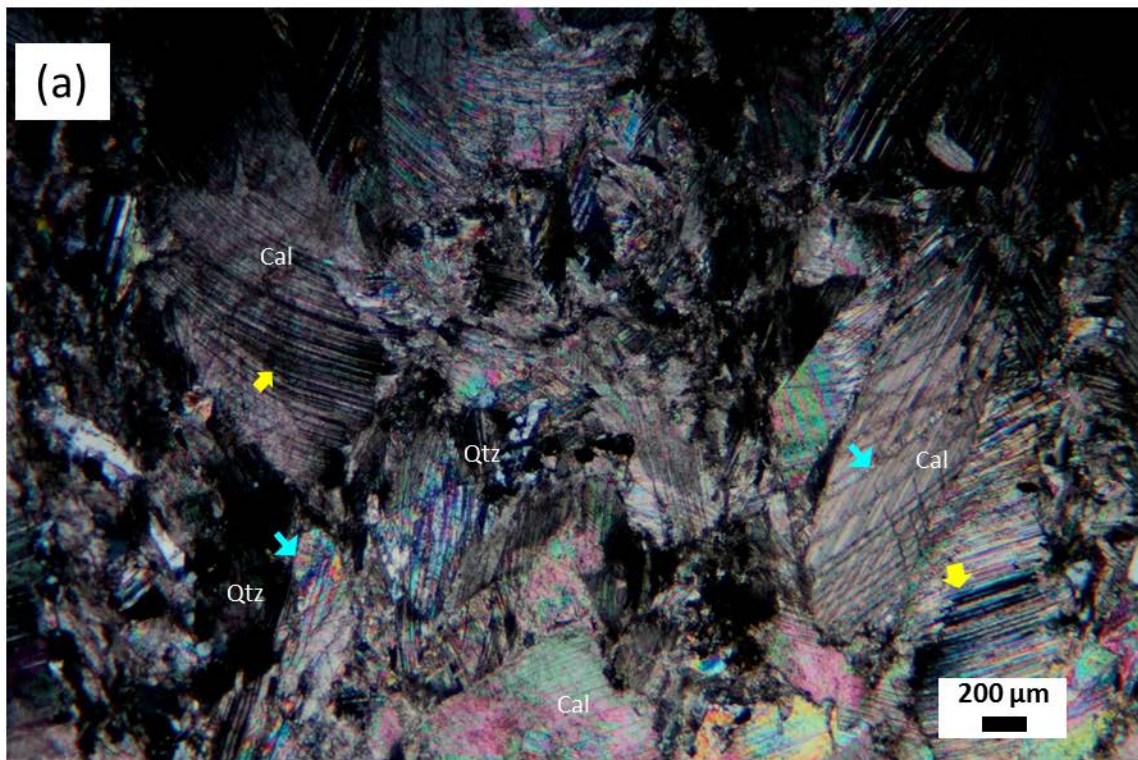




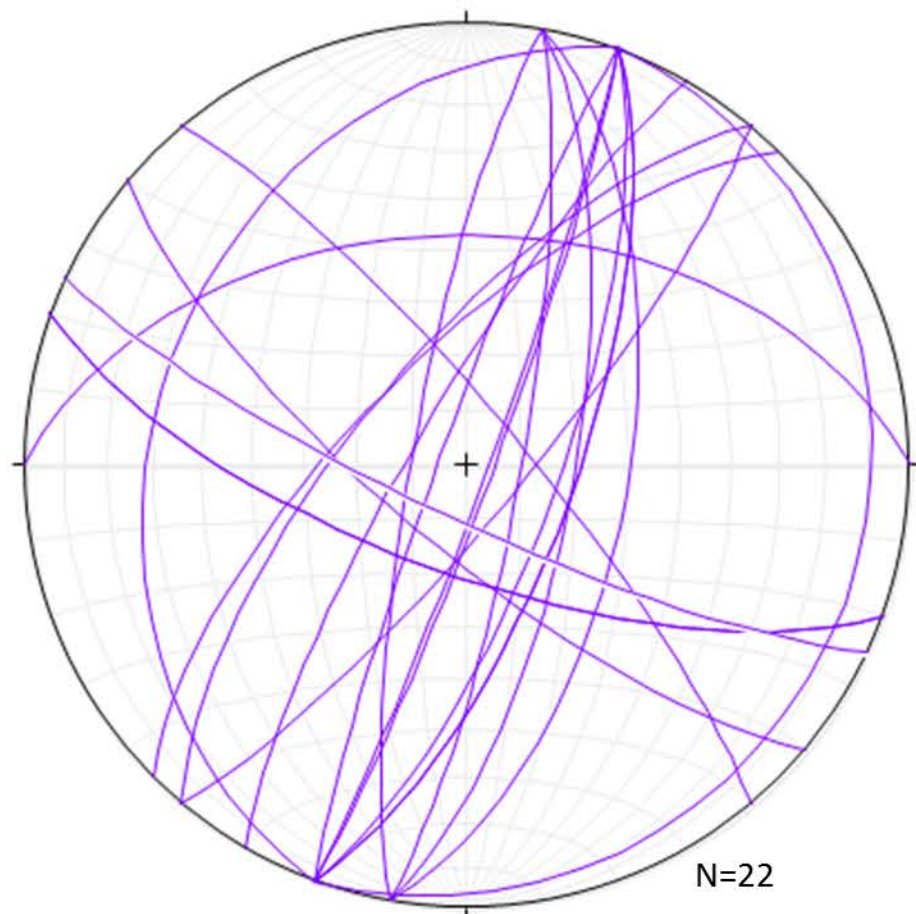




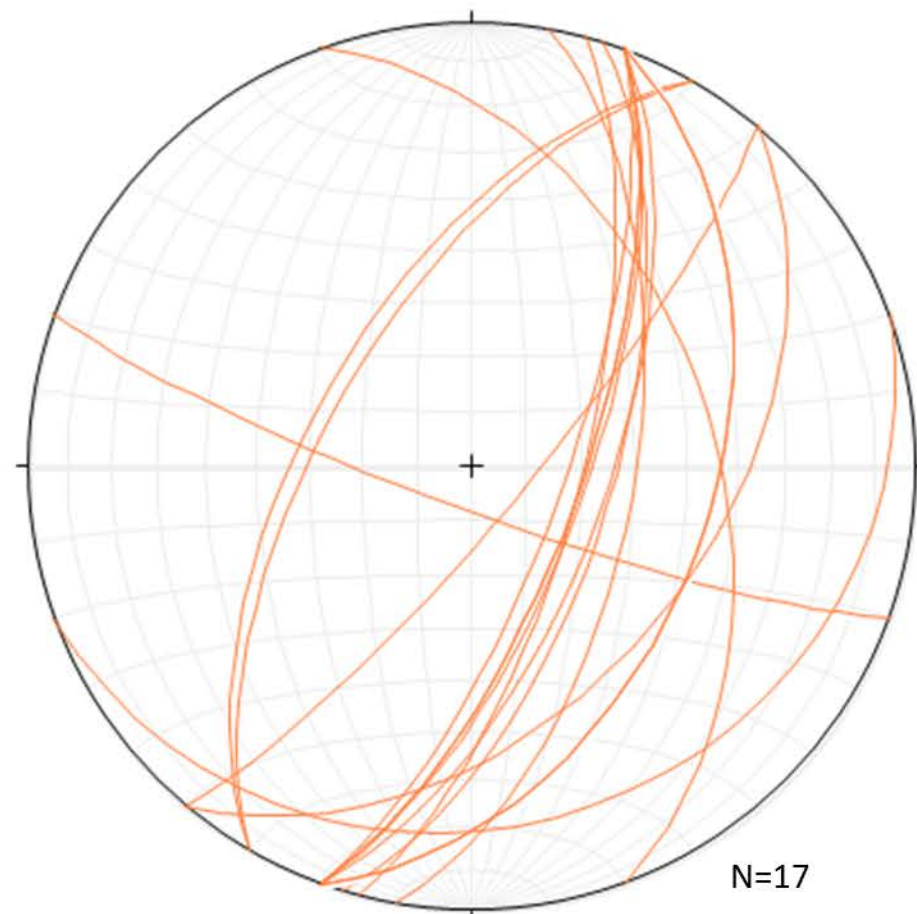




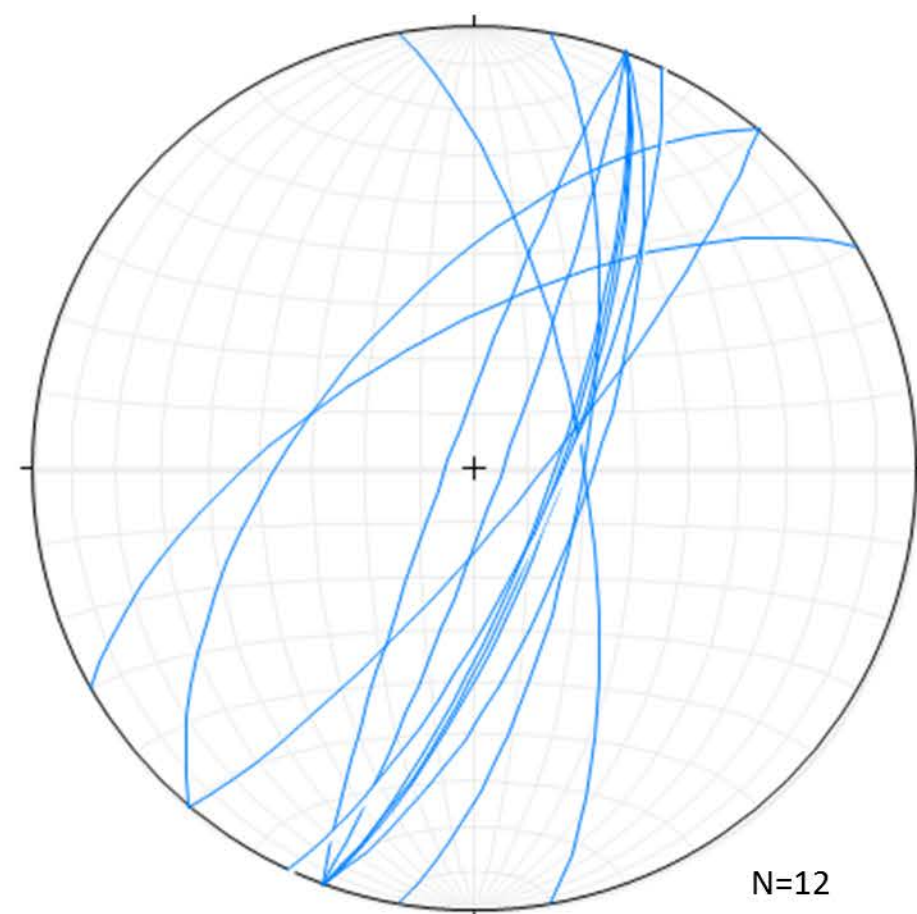




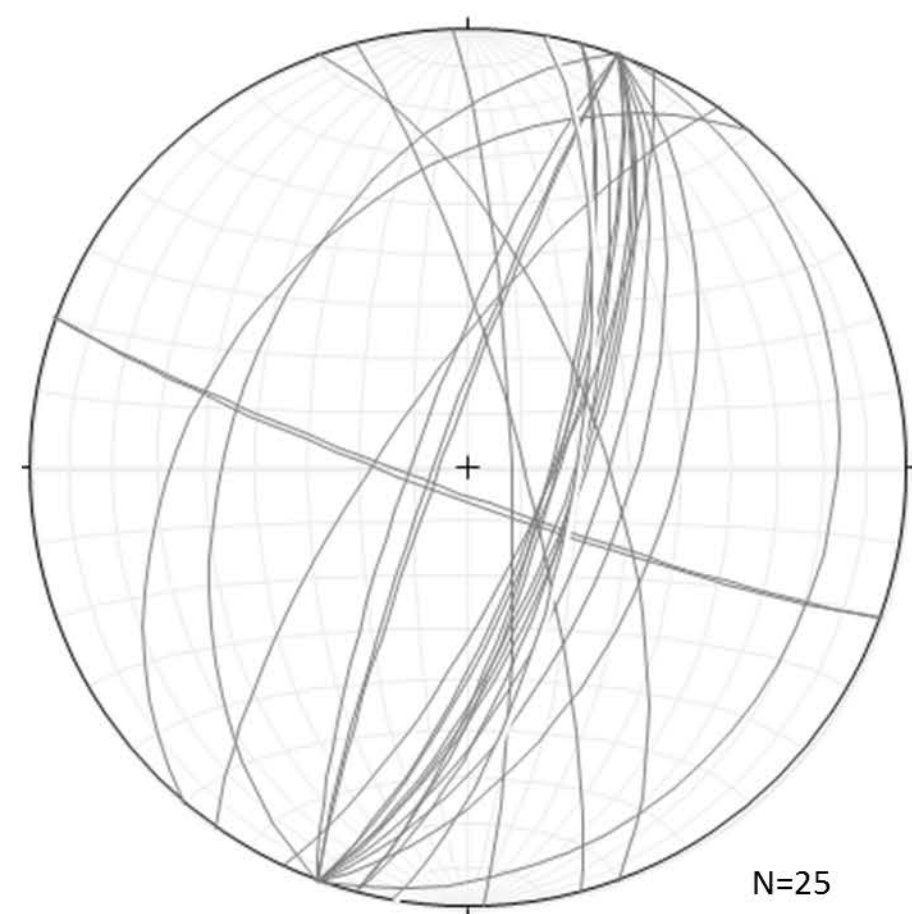
(a) Massive Calcite (With Quartz)



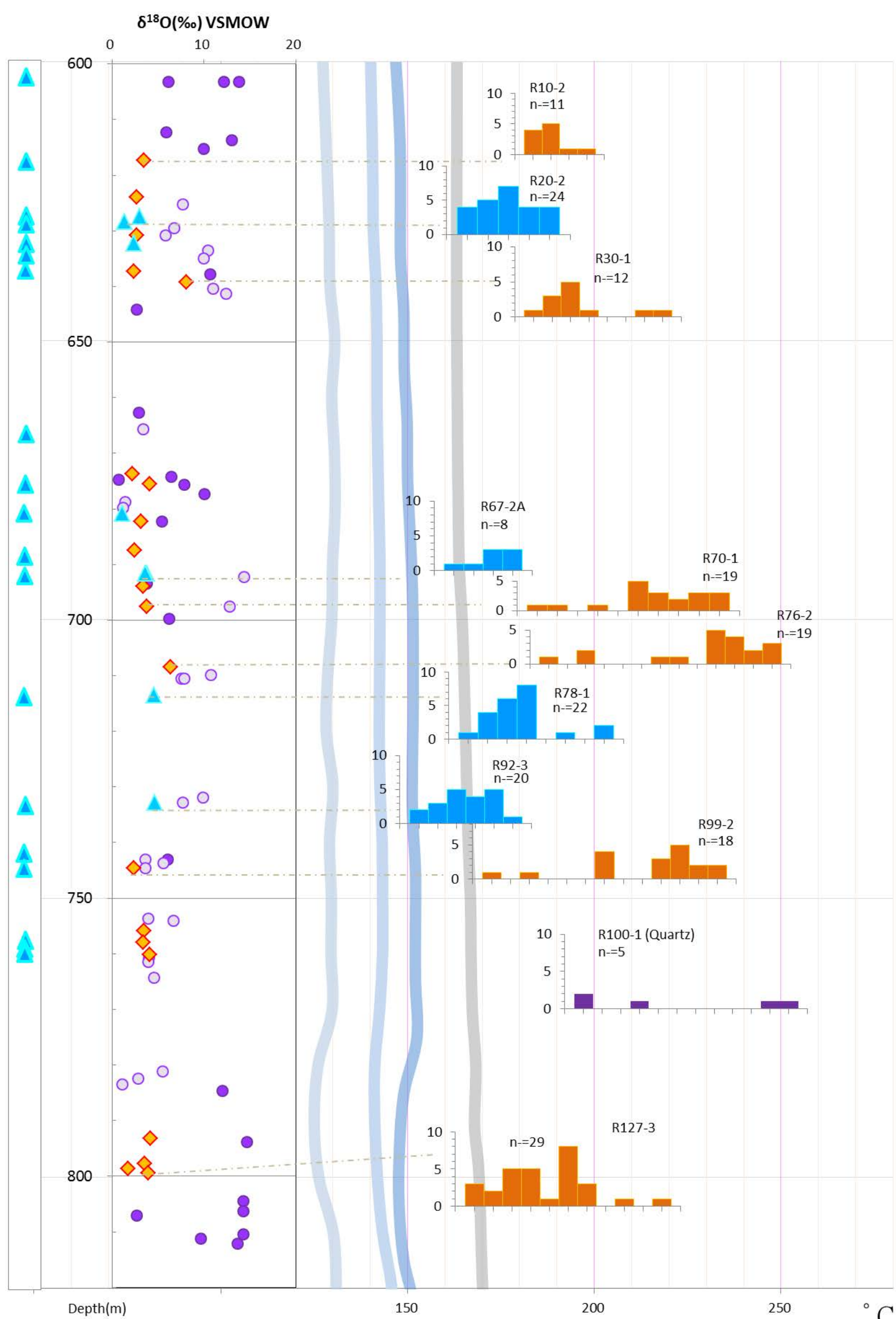
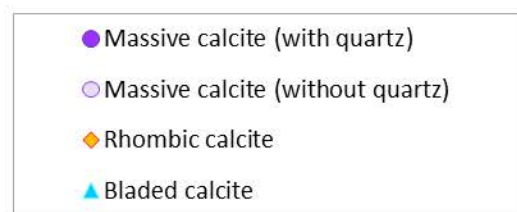
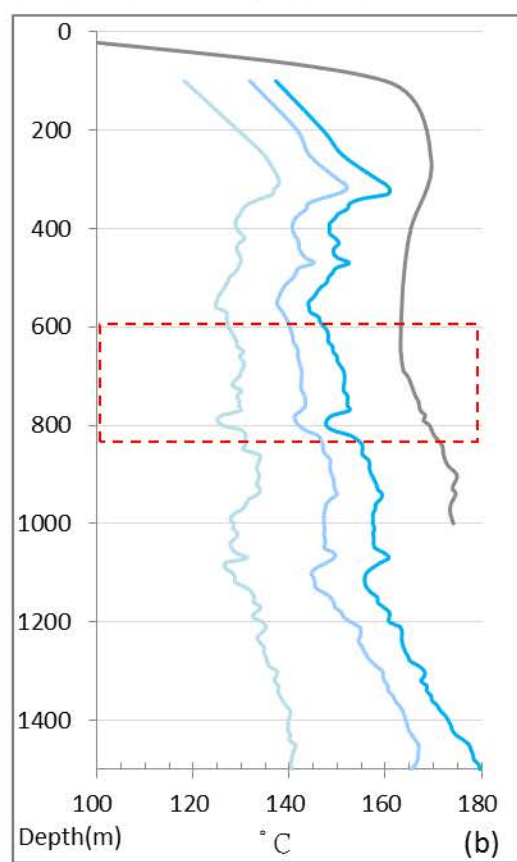
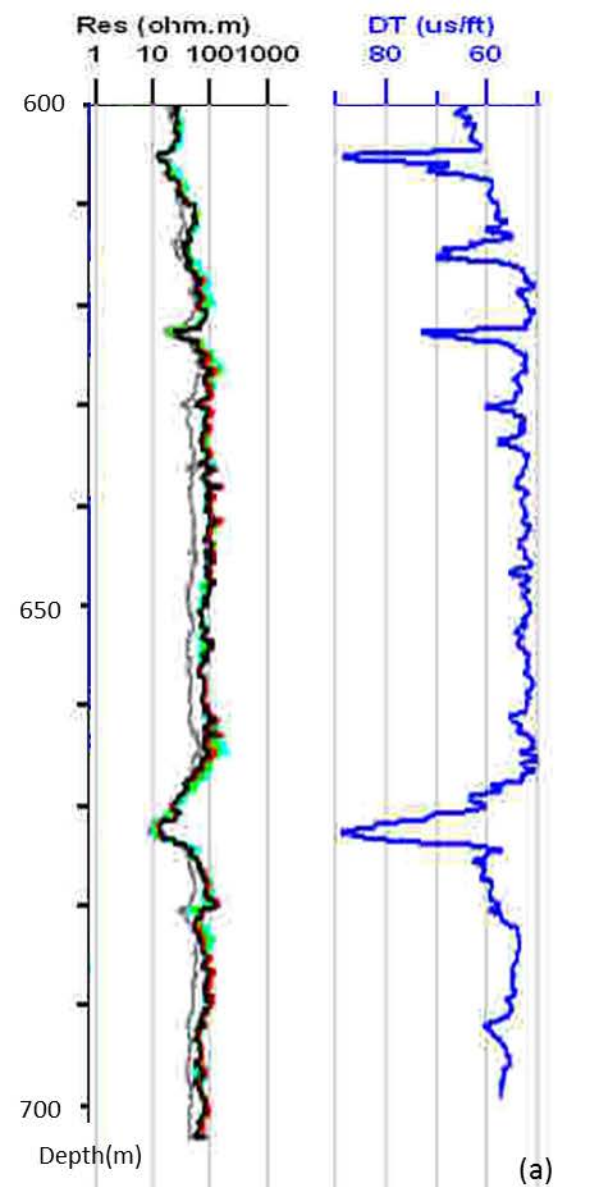
(b) Rhombic Calcite Crystal



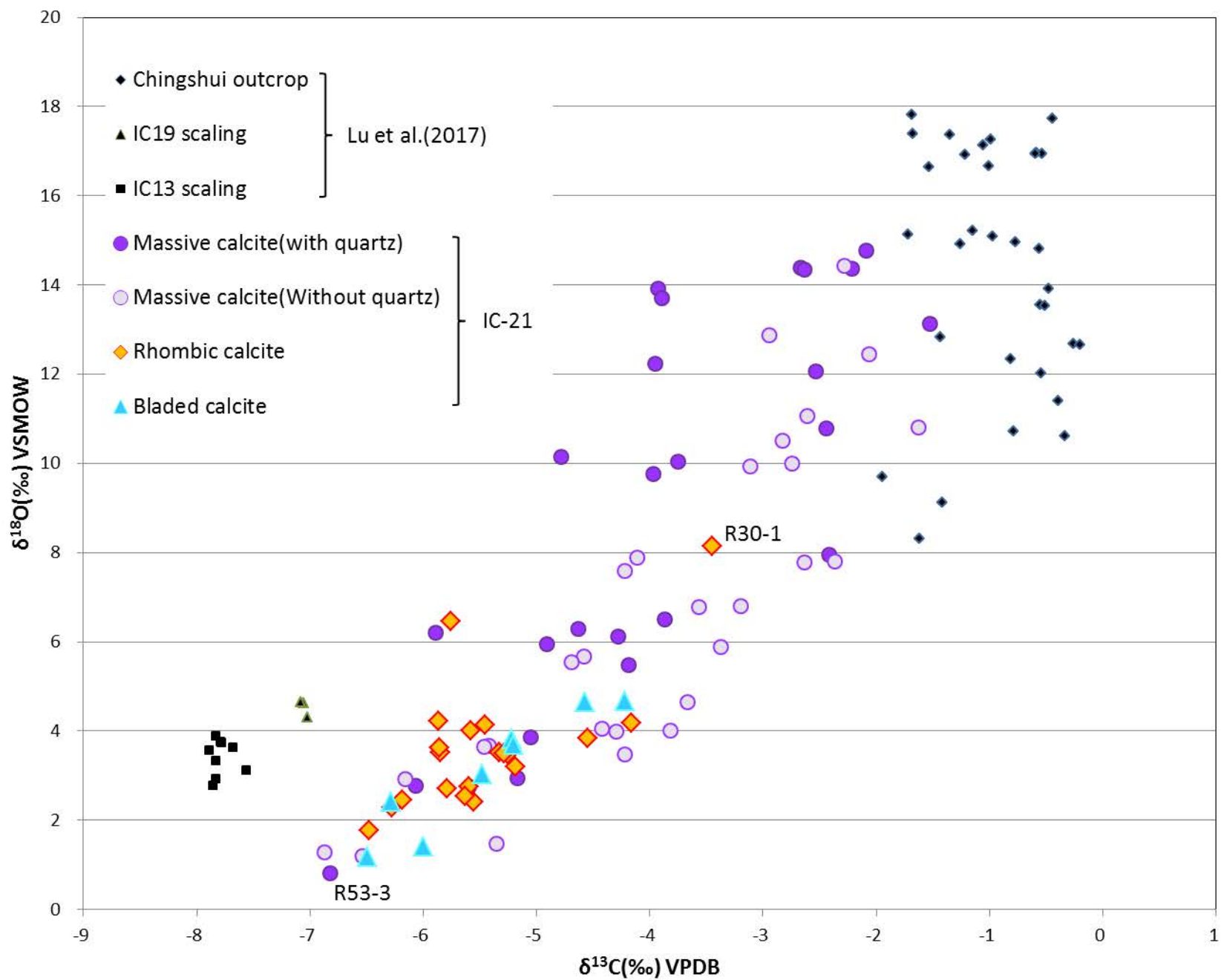
(c) Bladed Calcite

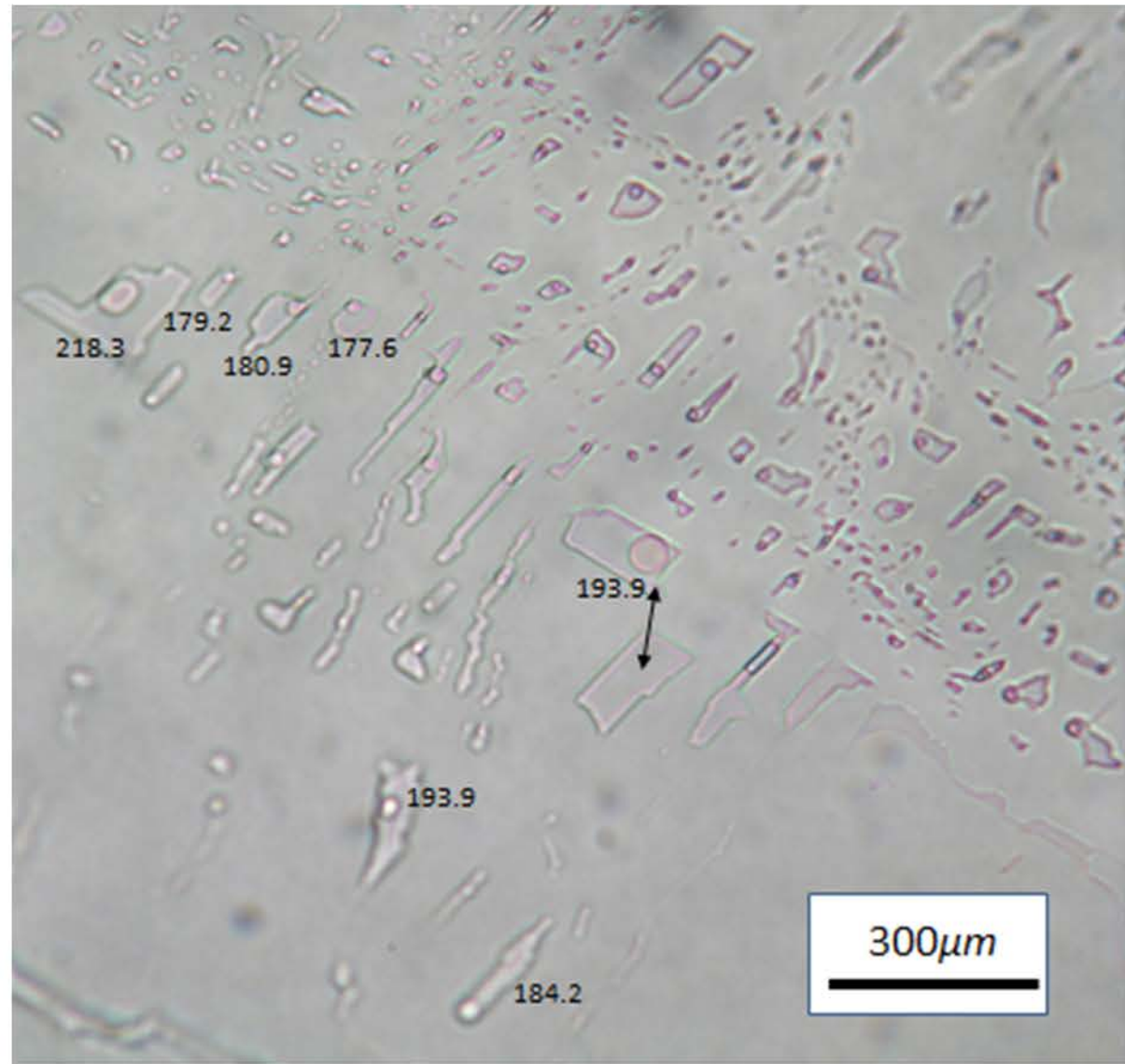
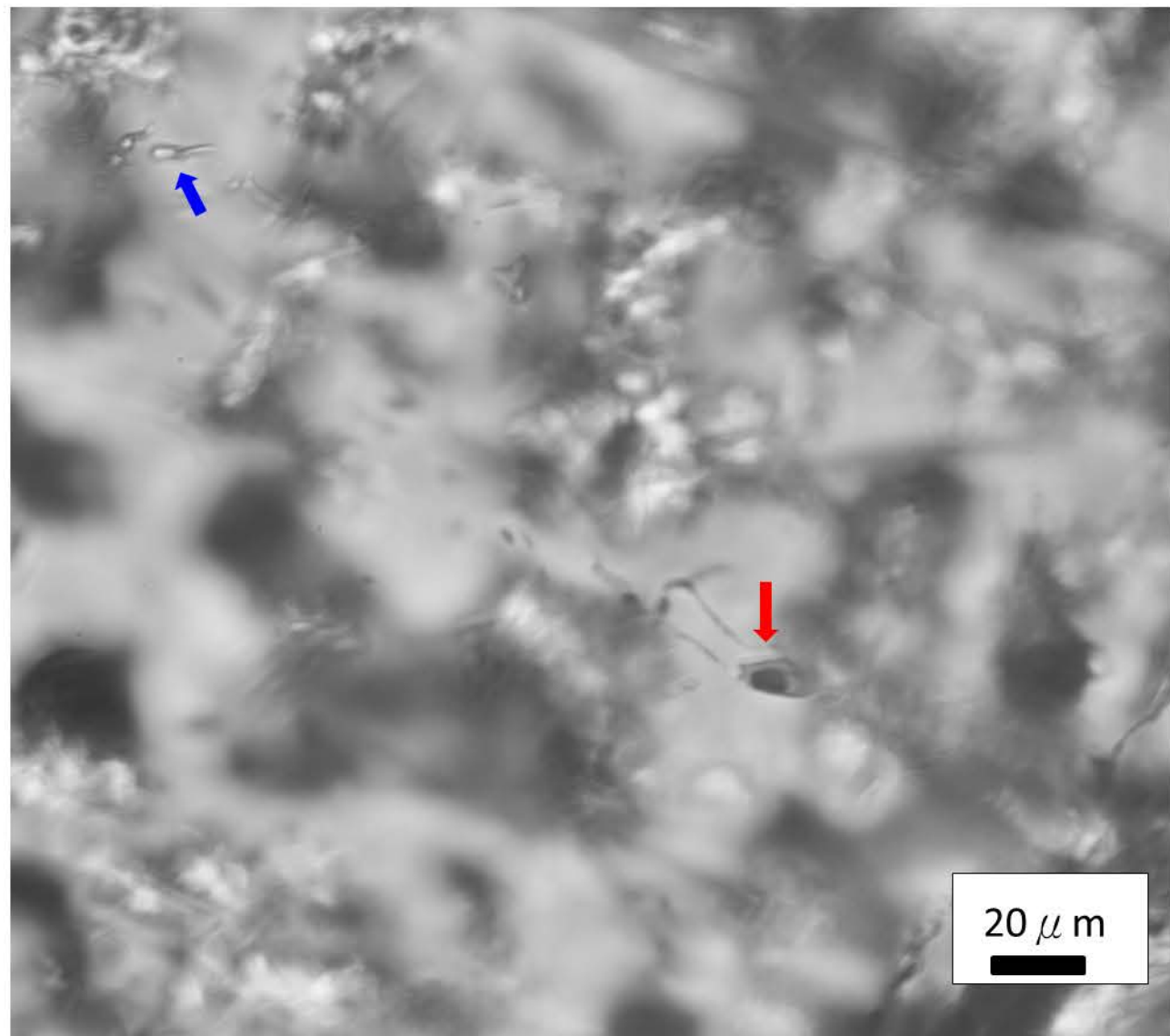


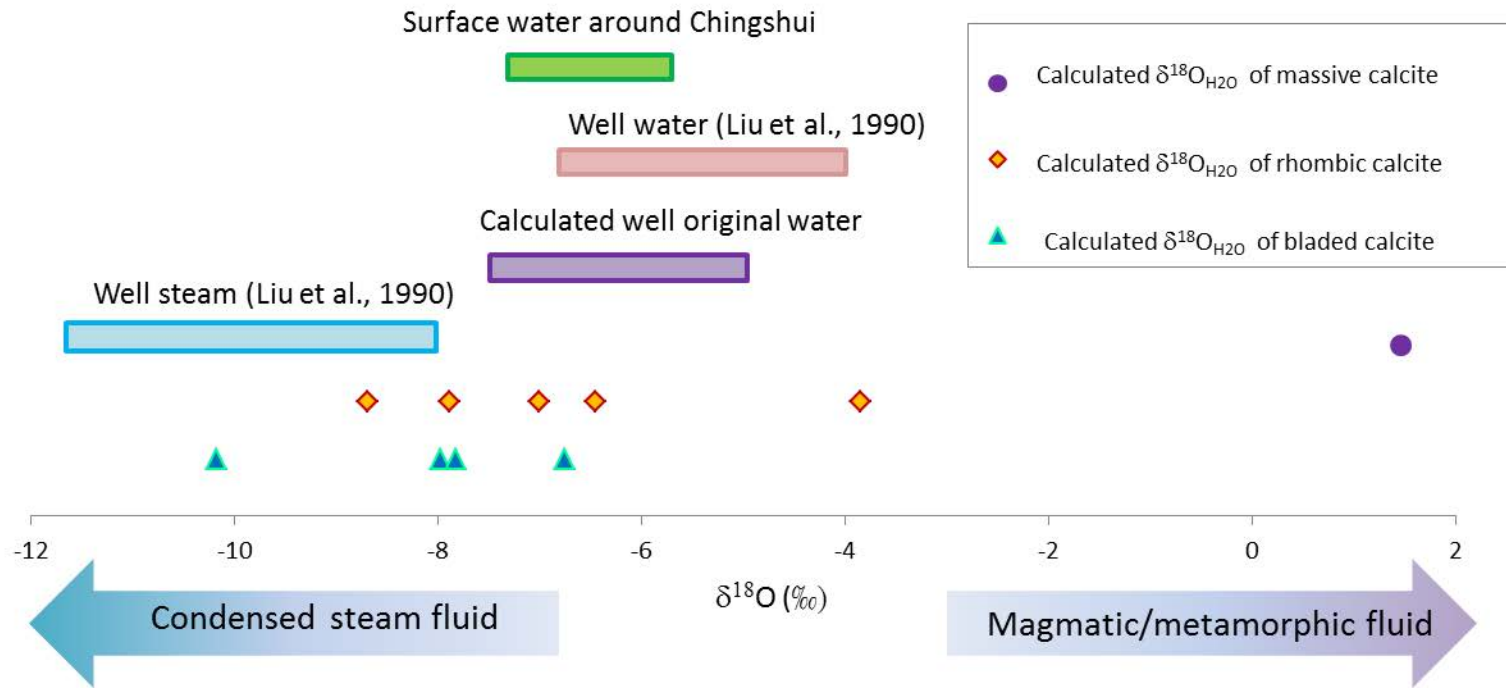
(d) Massive Calcite (Without Quartz)



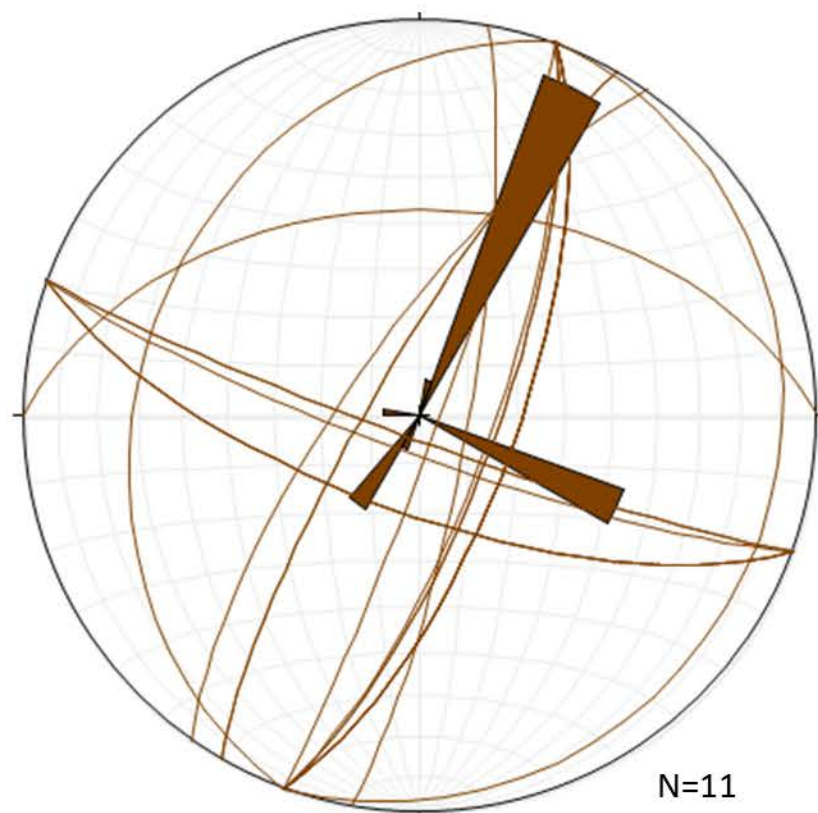




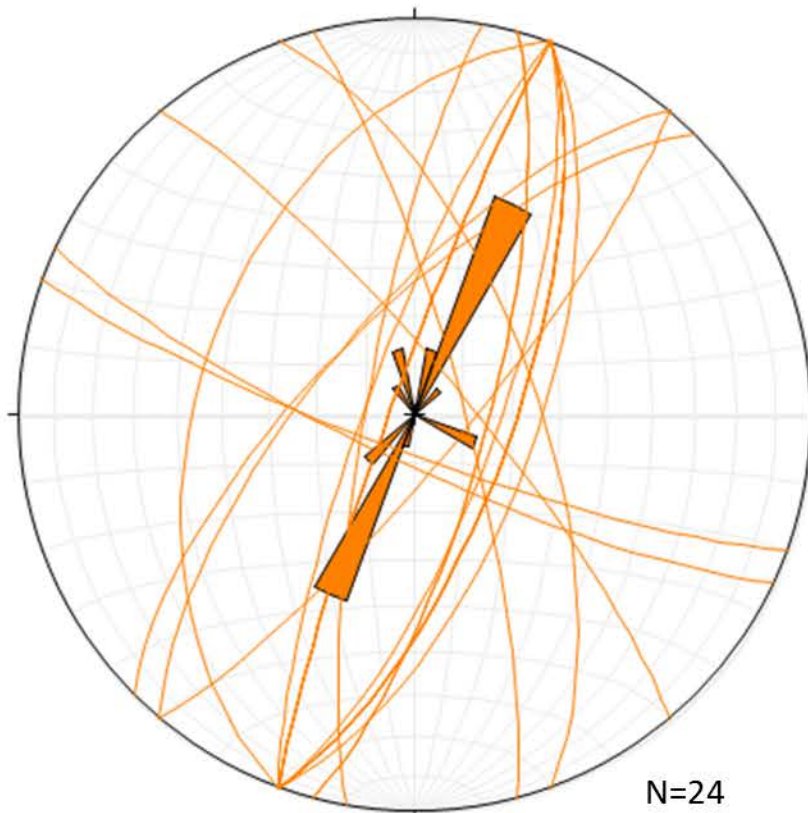




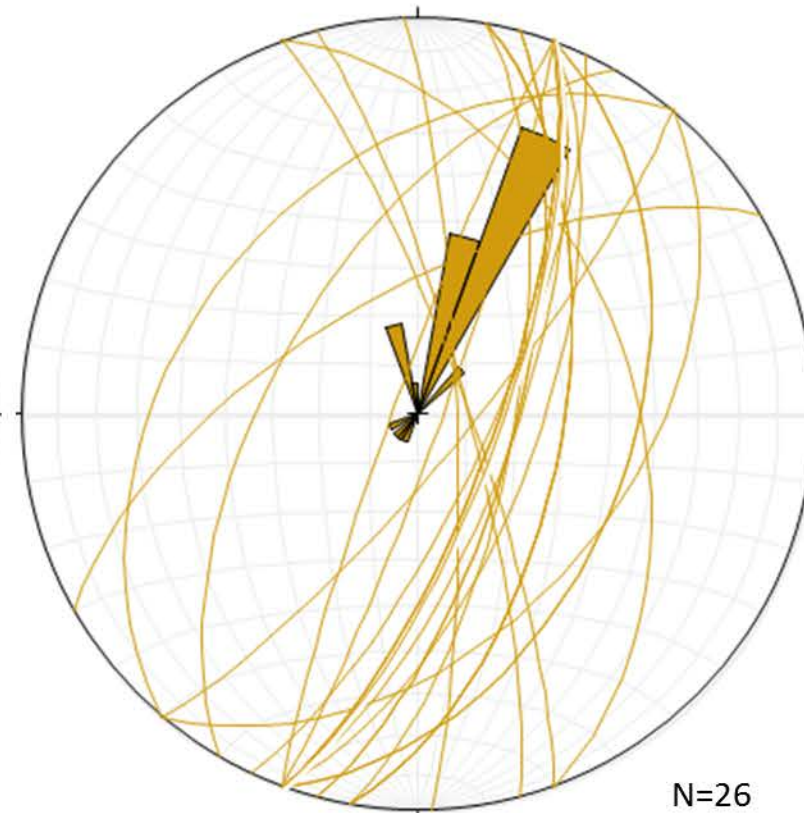




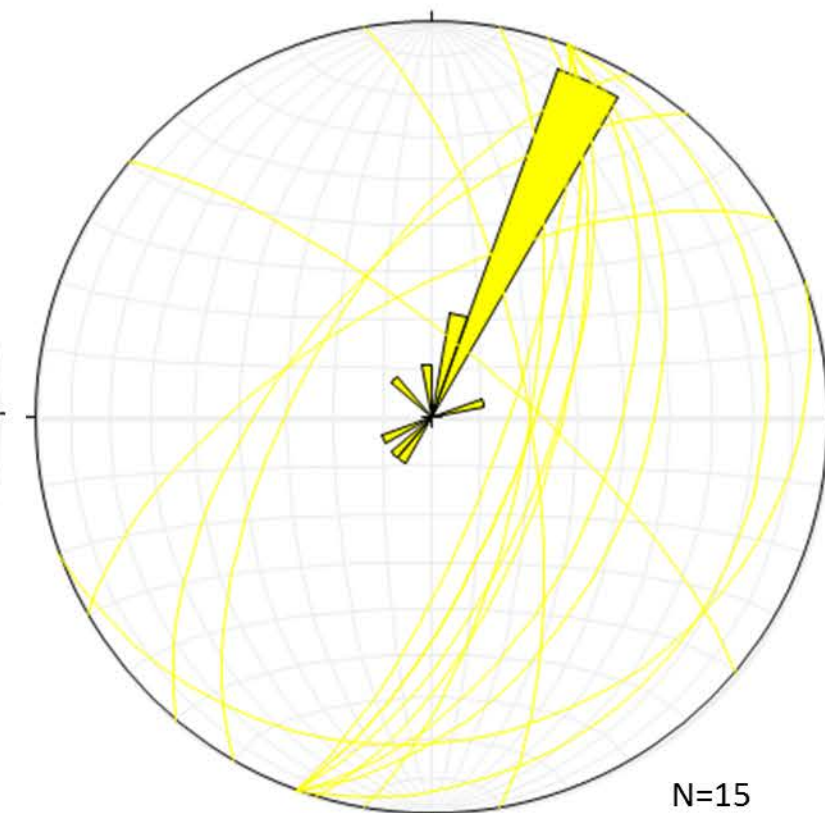
$\delta^{18}\text{O}$  values of calcite >10 ‰ VSMOW



$\delta^{18}\text{O}$  values of calcite 5-10 ‰ VSMOW



$\delta^{18}\text{O}$  values of calcite 3-5 ‰ VSMOW



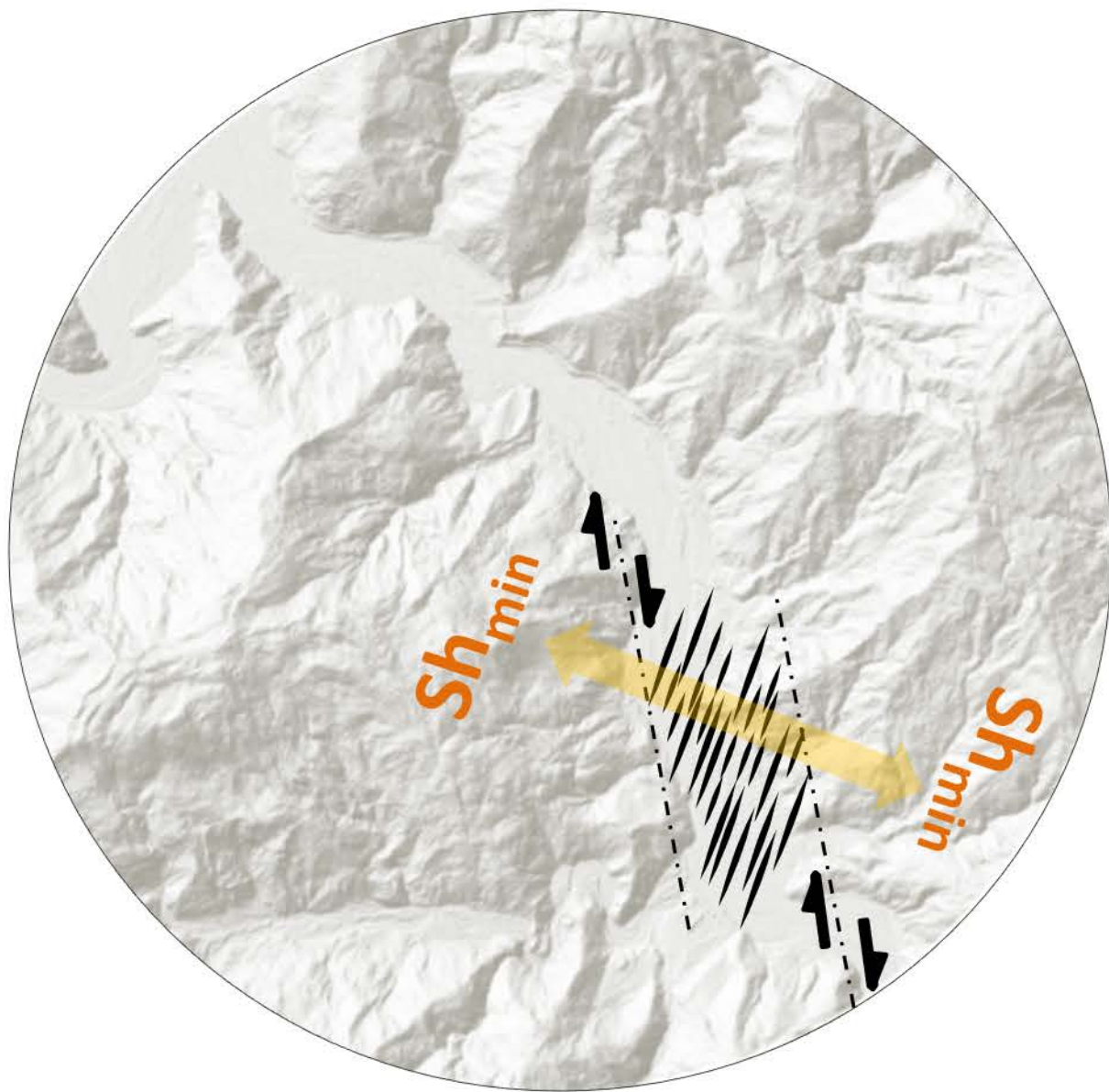
$\delta^{18}\text{O}$  values of calcite 0-3 ‰ VSMOW



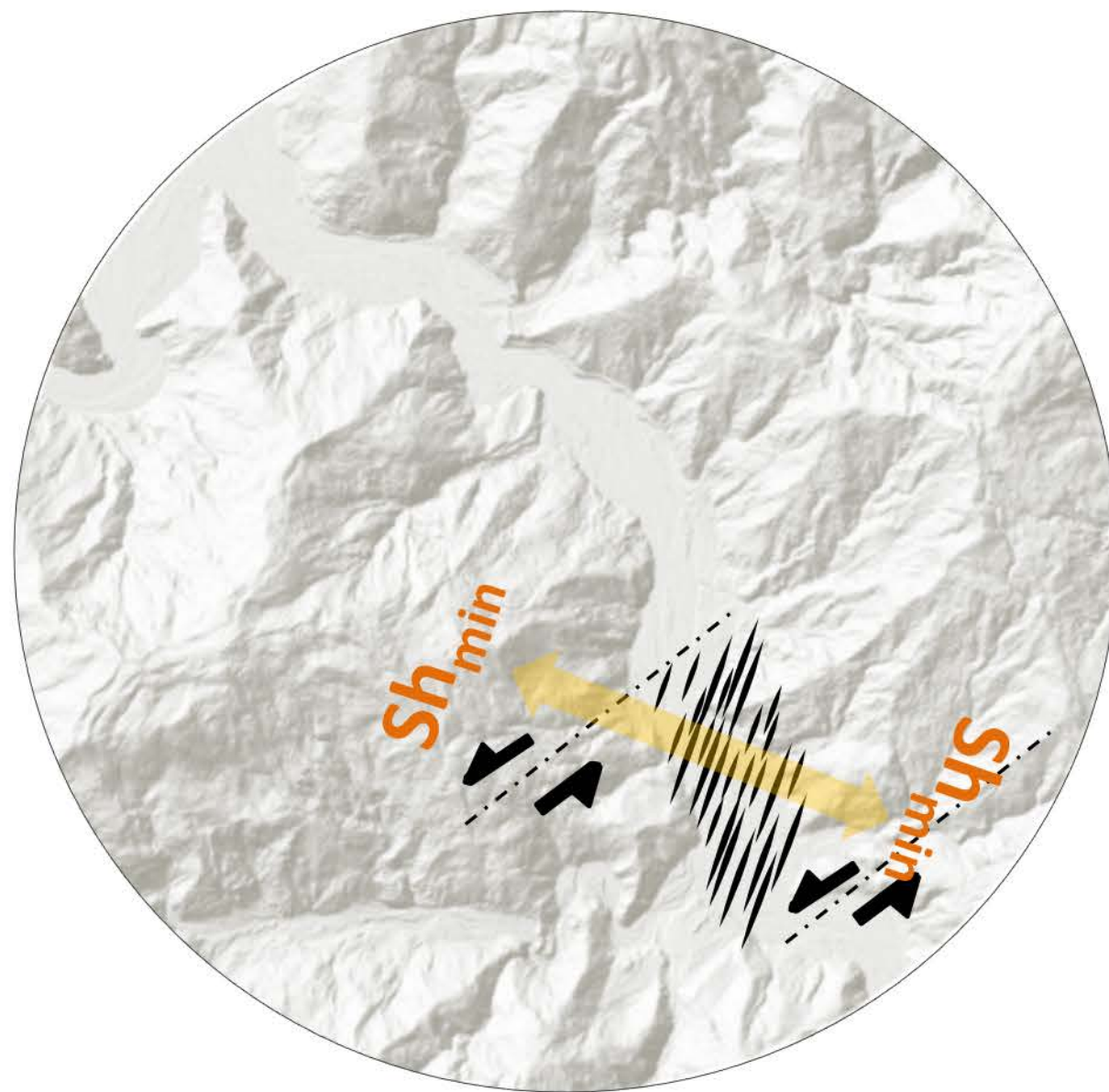
magmatic fluid sources

Meteoric fluid sources

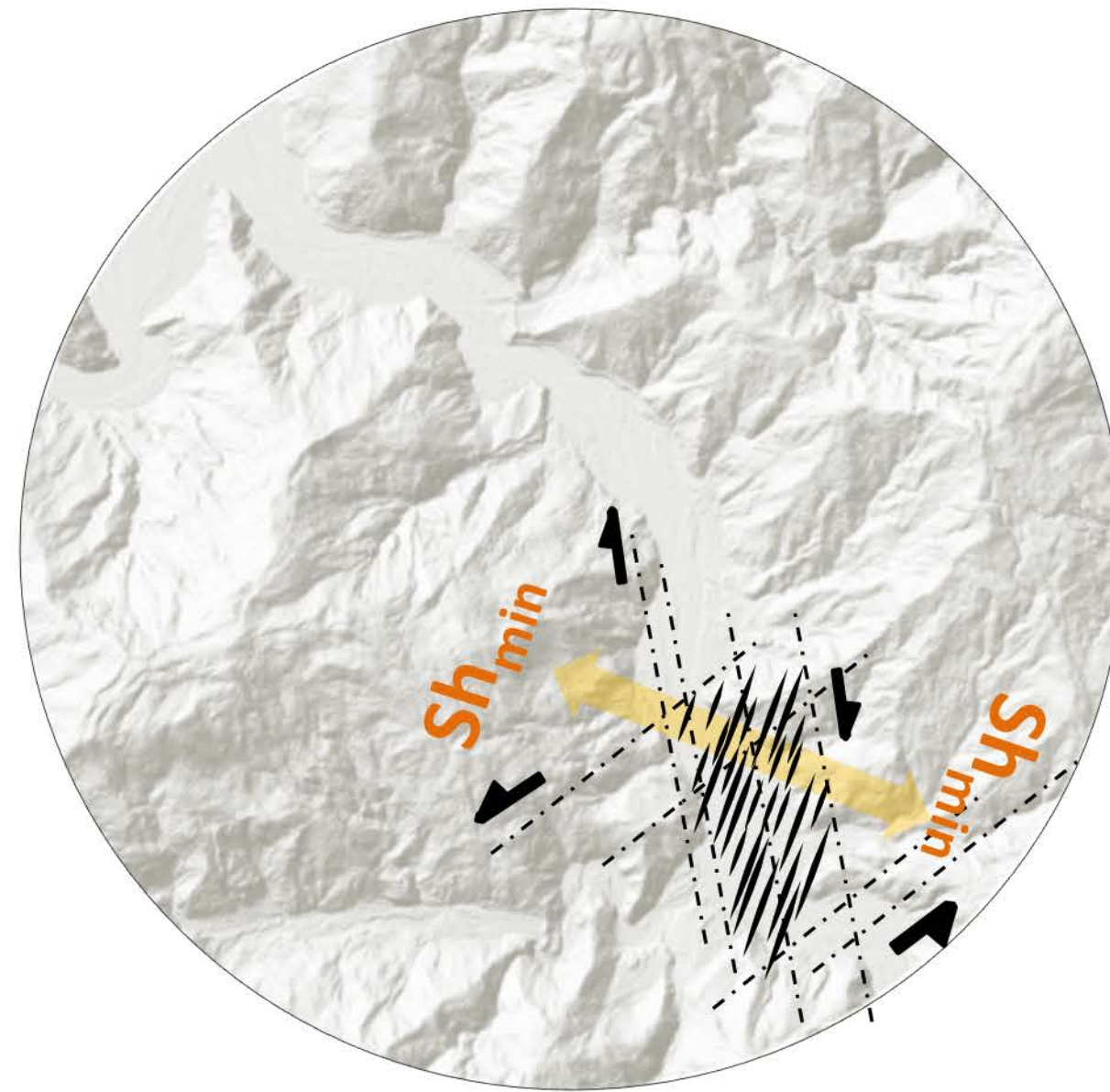




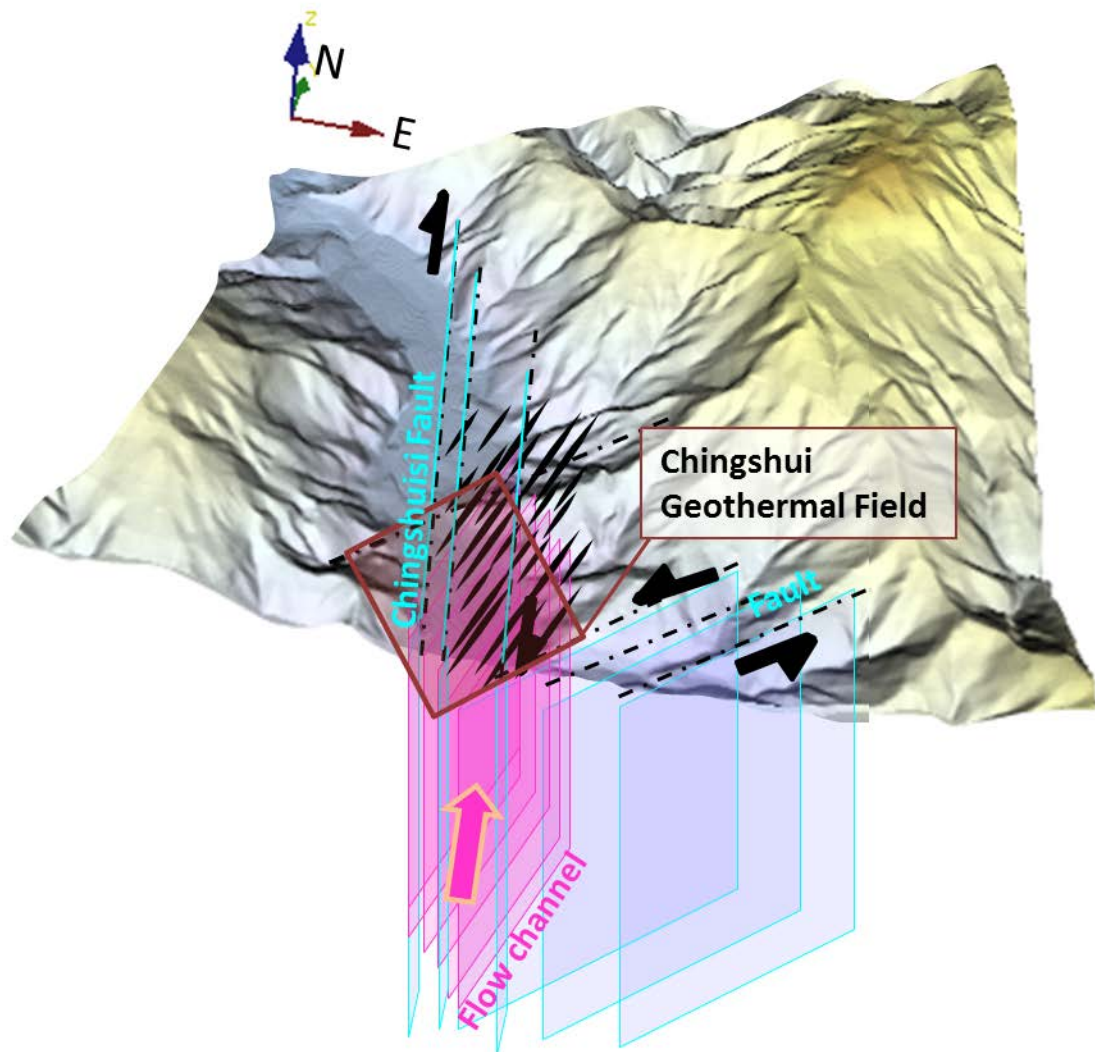
Model-A



Model-B



Model-A+B





Well No.	Bottom T (° C)	pH	HCO <sub>3</sub> <sup>-</sup> (ppm)	Cl <sup>-</sup> (ppm)	SO <sub>4</sub> <sup>2-</sup> (ppm)	SiO <sub>2</sub> (ppm)	Na <sup>+</sup> (ppm)	K <sup>+</sup> (ppm)	Ca <sup>2+</sup> (ppm)	Mg <sup>2+</sup> (ppm)	B (ppm)	H <sub>2</sub> O:NCG <sup>c</sup> (V%)	CO <sub>2</sub> in NCG (V%)
IC-04	201	8.8	2768	16	24	370	1149	36.0	1.0	0.8	31	-	-
IC-04	201	8.5	2619	18	32	342	1095	36.0	0.6	0.2	34	89.7 : 10.3	97.9
IC-21	175	9.0	1659	37	33	272	825	56.9	0.5	0	35	96.1 : 3.9	98.4
River	20	8.0	226			3.9	6.0	2.5	33	9.1	-	-	-

<sup>a</sup>The The data of IC-04 are from Lin(2000) and Liu et al. (1990)

<sup>b</sup>The The data of IC-21 are from ITRI (2012).

<sup>c</sup> NCG means non-codensible gases.

Replicates		$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$	Ave $\Delta 47$	S.E.	T ( ° C) <sup>a</sup>			$\text{d}^{18}\text{O}_{\text{H}_2\text{O}}$ <sup>b</sup>
	(n)	(‰,VPDB)	(‰,SMOW)	(‰,VPDB)	(‰,CDES)	(‰,CDES)	Error-	Error+		(‰,SMOW)
R55-1	2	-4.3	10.6	-19.7	0.415	0.001	208	13	14	1.5
R76-2	3	-5.8	7.1 <sup>c</sup>	-23.1	0.442	0.005	173	15	16	-4.0 <sup>d</sup>

<sup>a</sup>The calcite growth temperatures calculated from corrected D47 values are based on various theoretical and experimental calibrations derived by revised [Kluge et al.\(2015\)](#).

<sup>b</sup>The  $\delta^{18}\text{O}$  of fluids were estimated by [Friedman & O'Neil \(1977\)](#)

<sup>c</sup>The  $\delta^{18}\text{O}$  value is 7.1 ‰ VSMOW simultaneously measurement with clumped isotope, little higher than oxygen isotopic value of 6.5‰.

<sup>d</sup>. If the  $\delta^{18}\text{O}$  value of calcite is 6.5 ‰ VSMOW, then the  $\text{d}^{18}\text{O}_{\text{H}_2\text{O}}$  will be -4.6 ‰ VSMOW.

crystal forms	sample name	depth (m)	$\delta^{13}\text{C}(\text{‰})$ VPDB	$\delta^{13}\text{C}$ std.	$\delta^{18}\text{O}(\text{‰})$ VSMOW	$\delta^{18}\text{O}$ std.	Strike	Dip	TH of fluid inclusions(°C)	Calculated fluid value $\delta^{18}\text{O}$ (‰) VSMOW
Rhombic calcite crystal	R10-2	617.40	-5.8	0.01	3.5	0.02	210	60W	182-197	-7.0
Rhombic calcite crystal	R30-1C	639.25	-3.4	0.01	8.1	0.02	290	82S	184-216	-2.3
Rhombic calcite crystal	R70-1C	697.50	-4.5	0.01	3.8	0.02	20	70E	186-231	-6.5
Rhombic calcite crystal	R76-2	708.44	-5.8	0.02	6.5	0.02	20	70E	186-246	-3.8
Rhombic calcite crystal	R99-2C	744.59	-6.2	0.01	2.4	0.01	Hydrothermal breccia		172-235	-8.7
Rhombic calcite crystal	R127-3	797.73	-5.9	0.01	3.6	0.02	340	45E	166-218	-7.9
bladed calcite	R20-2C	628.37	-6.0	0.01	1.4	0.01	240	65W	165-189	-10.2
bladed calcite	R67-2A	691.65	-5.2	0.01	3.8	0.01	20	74E	162-179	-8.0
bladed calcite	R78-1	713.47	-4.6	0.00	4.6	0.01	20	85E	168-201	-6.8
Platy calcite	R92-3C	732.87	-4.2	0.00	4.7	0.04	200	85W	152-178	-7.8
Quartz	R100-1	745.70	-	-	-	-	80	55E	179-254	